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OF

## THE CHEMICAL SOCIETY.

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ON

### ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

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# INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

## NOMENCLATURE AND SYSTEM OF NOTATION

### ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.
7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

(b) That formulae should be shortened by the judicious employment of the symbols Me for  $\text{CH}_3$ , Et for  $\text{C}_2\text{H}_5$ , Pr<sup>n</sup> for  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ , Pr<sup>s</sup> for  $\text{CH}(\text{CH}_3)_2$ , Ph for  $\text{C}_6\text{H}_5$ , Py for  $\text{C}_5\text{H}_4\text{N}$ , Ac for  $\text{CO}\cdot\text{CH}_3$ , and Bz for  $\text{CO}\cdot\text{C}_6\text{H}_5$ .

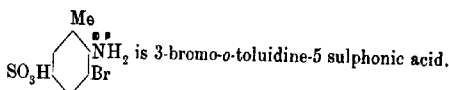
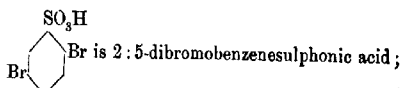
(c) That formulae should be written in *one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

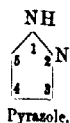
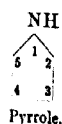
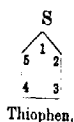
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1:2- or ortho-, 1:3- or meta-, and 1:4- or para-.

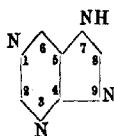
(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example:—

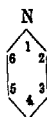


29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulae should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical:—





Purine.\*



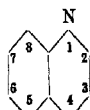
Pyridine.



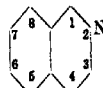
Indole.



Naphthalene.



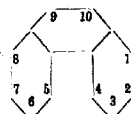
Quinoline.



isoQuinoline.



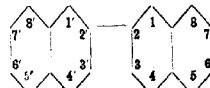
Anthracene.



Phenanthrene.



Diphenyl.

 $\beta$ -Dinaphthyl.**Manuscript.**

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 x 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

**Proofs.**

34. Abstractors are expected to read and correct proofs carefully, and to check all formulae and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

\* \* The Editor's decision, in all matters connected with the Abstracts, must be considered final.

\* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

*List of Symbols Recommended by the Working Committee of the International Commission for the Unification of Physico-chemical Symbols (1914). [See Trans., 1921, 119, 502—512.]*

1. *Mathematical Symbols.*

|  | Usual symbol. | Alternative symbol. |
|--|---------------|---------------------|
| Base of natural (Napierian) logarithms ... | $e$           |                     |
| Diameter .....                             | $d$           |                     |
| Radius .....                               | $r$           |                     |
| Ratio of circumference to diameter .....   | $\pi$         |                     |
| Summation .....                            | $\Sigma$      |                     |
| Variation .....                            | $\delta$      |                     |
| Total differential .....                   | $d$           |                     |
| Partial differential .....                 | $\partial$    |                     |

2. *Universal Constants.*

|   |     |  |
|---|-----|--|
| Acceleration due to gravity .....   | $g$ |  |
| Mechanical equivalent of heat .....   | $J$ |  |
| Avogadro's constant [number of molecules in 1 gram-molecule (mole)] .....   | $N$ |  |
| Gas constant per mole .....   | $R$ |  |
| Faraday's constant (number of coulombs per gram-equivalent of an ion) ..... | $F$ |  |
| Charge on an electron .....   | $e$ |  |

3. *General Physics and Chemistry.*

|   |  |  |
|---|--|--|
| Length .....  | $l$  |  |
| Height .....  | $h$  |  |
| Mass .....  | $m$  |  |
| Time .....  | $t$  |  |
| Volume .....  | $v, V$   |  |
| Density (mass per unit volume) .....  | $d$  |  |
| Pressure .....  | $p, P$   |  |
| Concentration .....   | $c, C$   |  |
| Mole fraction .....   | $x$  |  |
| Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density ..... | $\left\{ \begin{array}{l} p_c, v_c, \\ t_c, T_c, \\ d_c \end{array} \right.$ |  |
| Reduced quantities: pressure, volume, temperature, density .....                                      | $\left\{ \begin{array}{l} p_r, v_r, \\ t_r, T_r, \\ d_r \end{array} \right.$ |  |
| van der Waals's constants .....   | $a, b$   |  |
| Fluidity .....  | $\phi$   |  |
| Viscosity .....   | $\eta$   |  |
| Surface tension .....   | $\gamma$   |  |
| Diffusion coefficient .....   | $\Delta$   |  |
| Atomic weight .....   | $A$  |  |
| Molecular weight .....  | $M$  |  |
| Velocity coefficient of reaction .....  | $k$  |  |
| Equilibrium constant .....  | $K, (K_c, K_p)$  |  |
| van't Hoff coefficient .....  | $i$  |  |
| Degree of dissociation (electrolytic, thermal, etc.) .....  |  |  |

*D*

## 4. Heat and Thermodynamics.

|  | Usual<br>symbol. | Alternative<br>symbol. |
|--|------------------|------------------------|
| Temperature (centigrade) .....                 | $t$              | $\theta$               |
| Temperature (absolute) .....                   | $T$              |                        |
| Critical temperature .....                     | $t_c, T_c$       |                        |
| Reduced temperature .....                      | $t_r, T_r$       |                        |
| Critical solution temperature .....            | $t_{cs}, T_{cs}$ |                        |
| Quantity of heat .....                         | $Q$              |                        |
| Entropy .....                                  | $S$              |                        |
| Specific heat .....                            | $c$              |                        |
| Specific heat at constant pressure .....       | $c_p$            |                        |
| Specific heat at constant volume .....         | $c_v$            |                        |
| Ratio of specific heats, $c_p : c_v$ .....     | $\gamma$         |                        |
| Molecular heat .....                           | $C$              |                        |
| Molecular heat at constant pressure .....      | $C_p$            |                        |
| Molecular heat at constant volume .....        | $C_v$            |                        |
| Latent heat per gram .....                     | $l$              |                        |
| Latent heat per mole .....                     | $L$              |                        |
| Maximum work (diminution of free energy) ..... | $A$              |                        |

## 5. Optics.

|  |   |  |
|--|---|--|
| Wave-length of light .....                           | $\lambda$   |  |
| Refractive index .....                               | $n$   |  |
| Specific refractive power (Gladstone and Dale) ..... | $\sigma_s, [\sigma_s]_d$  |  |
| Specific refractive power (Lorentz and Lorenz) ..... | $\sigma_L, [\sigma_L]_d$  |  |
| Molecular refractive power .....                     | $\left\{ \begin{array}{l} R_g, R_L \\ [R_g]_d, [R_L]_d \end{array} \right.$ |  |
| Angle of optical rotation .....                      | $\alpha$  |  |
| Specific rotatory power .....                        | $[\alpha]$  |  |
| Molecular rotatory power .....                       | $M[\alpha]$   |  |
| Specific magnetic rotation .....                     | $[\omega]$  |  |
| Molecular magnetic rotation .....                    | $M[\omega]$   |  |

## 6. Electricity and Magnetism.

|   |  |  |
|---|--|--|
| Quantity of electricity .....   | $Q$  |  |
| Current intensity .....   | $I$  |  |
| Resistance .....  | $R$  |  |
| Electromotive force .....   | $E$  |  |
| Electrode potential, or discharge potential of an ion .....   | $E$  |  |
| Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero .....   | $E_h, E_c$                                     |  |
| Normal potential, i.e., the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration ..... | ${}^nE_h, {}^nE_c$                             |  |
| Dielectric constant .....   | $\epsilon$                                     |  |
| Conductivity (specific conductance) .....   | $\kappa$                                       |  |
| Equivalent conductivity .....   | $\Lambda$                                      |  |
| Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent .....   | $\Lambda_{10}, \Lambda_{20}, \Lambda_{\infty}$ |  |

## 6. Electricity and Magnetism—(continued).

|  | Usual symbol.          | Alternative symbol. |
|--|------------------------|---------------------|
| Equivalent conductivity of kation and of anion .....   | $\Lambda_k, \Lambda_a$ |                     |
| Equivalent conductivity of specified ions...   | $\Lambda_K, \Lambda_A$ |                     |
| Molecular conductivity .....   | $\mu$                  |                     |
| Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm. .... | $U_k, U_a$             |                     |
| Transport number of kation and of anion ...  | $n_k, n_a$             |                     |
| Magnetic permeability .....  | $\mu$                  |                     |
| Magnetic susceptibility .....  | $\kappa$               |                     |

*List of Symbols, Arranged Alphabetically.*

| Symbol.            | Name of quantity.   |
|--------------------|---|
| $A$                | Atomic weight; maximum work.  |
| $a$                | Van der Waals's constant.   |
| $b$                | Van der Waals's constant.   |
| $C$                | Concentration; molecular heat.  |
| $c$                | Concentration; specific heat.   |
| $C_p, C_v$         | Molecular heat at constant pressure, and at constant volume.  |
| $c_p, c_v$         | Specific heat at constant pressure, and at constant volume.   |
| $D$                | Alternative symbol for density.   |
| $d$                | Diameter; total differential; density.  |
| $d_c$              | Critical density.   |
| $d_r$              | Reduced density.  |
| $E$                | Electromotive force; electrode potential.   |
| $e$                | Base of Napierian logarithms; charge on an electron.  |
| $E_h, E_s$         | Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.   |
| ${}_0E_h, {}_0E_s$ | Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration. |
| $F$                | Faraday's constant (number of coulombs per gram-equivalent of an ion).  |
| $g$                | Acceleration due to gravity.  |
| $h$                | Height.   |
| $I$                | Current.  |
| $i$                | Van't Hoff's coefficient.   |
| $J$                | Mechanical equivalent of heat.  |
| $K$                | Equilibrium constant.   |
| $K_m, K_p$         | Equilibrium constant, when molar concentrations and partial pressures respectively are employed.  |
| $k$                | Velocity coefficient of reaction.   |
| $L$                | Latent heat per mole.   |
| $l$                | Length; latent heat per gram.   |
| $M$                | Molecular weight.   |
| $M[\alpha]$        | Molecular rotatory power.   |
| $M[\omega]$        | Molecular magnetic rotatory power.  |
| $m$                | Mass.   |
| $N$                | Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.   |
|                    | Refractive index.   |

*List of Symbols, Arranged Alphabetically—(continued).*

| Symbol.                                     | Name of quantity.   |
|---|---|
| $n_+, n_-$                                  | Transport number of kation and of anion.  |
| $n_r$                                       | Refractive index (alternative symbol).  |
| $P$   | Pressure.   |
| $p$   | Pressure.   |
| $p_0, p_r$                                  | Critical pressure : reduced pressure.   |
| $Q$   | Quantity of heat; quantity of electricity.  |
| $R$   | Gas constant per mole; electrical resistance.   |
| $R_0, R_L$                                  | Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.  |
| $r$   | Radius.   |
| $r_0, r_L$                                  | Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.  |
| $S$   | Entropy.  |
| $T$   | Absolute temperature.   |
| $T_c$                                       | Critical temperature (on the absolute scale).   |
| $T_r$                                       | Reduced temperature (absolute).   |
| $T_{cs}$                                    | Critical solution temperature (absolute).   |
| $t$   | Time; temperature (centigrade).   |
| $t_c$                                       | Critical temperature (centigrade).  |
| $t_{cs}$                                    | Critical solution temperature (centigrade).   |
| $t_r$                                       | Reduced temperature (centigrade).   |
| $U_+, U_-$                                  | Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.   |
| $V$   | Volume.   |
| $v$   | Volume.   |
| $v_0, v_r$                                  | Critical volume : reduced volume.   |
| $W$   | Electrical resistance (alternative symbol).   |
| $x$   | Mole fraction.  |
| $\alpha$                                    | Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.  |
| $[\alpha]$                                  | Specific rotatory power.  |
| $\gamma$                                    | Surface tension; ratio of specific heats.   |
| $\Delta$                                    | Diffusion coefficient.  |
| $\delta$                                    | Variation.  |
| $\partial$                                  | Partial differential.   |
| $\epsilon$                                  | Electrode potential (alternative symbol); dielectric constant.  |
| $\epsilon_+, \epsilon_-$                    | Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).  |
| $\epsilon^+, \epsilon^-, \epsilon^0$        | Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols). |
| $\eta$                                      | Viscosity.  |
| $\theta$                                    | Temperature (centigrade), (alternative symbol).   |
| $\kappa$                                    | Specific conductance (conductivity); magnetic susceptibility.   |
| $\Lambda$                                   | Equivalent conductivity.  |
| $\Lambda_{10}, \Lambda_m, \Lambda_{\infty}$ | Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).  |
| $\Lambda_k, \Lambda_a$                      | Equivalent conductivity of kation and of anion.   |
| $\lambda$                                   | Wave-length of light.   |
| $\mu$                                       | Molecular conductivity; magnetic permeability.  |
| $\pi$                                       | Ratio of circumference to diameter.   |
| $\Sigma$                                    | Summation.  |
| $\sigma$                                    | Surface tension (alternative symbol).   |
| $\phi$                                      | Fluidity.   |
| $[\omega]$                                  | Specific magnetic rotation.   |

## JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

| ABBREVIATED TITLE.  | JOURNAL.   |
|---|--|
| <i>Abh. Böhm. Akad.</i> . . .                                 | Abhandlungen der Böhmischen Akademie.  |
| <i>Abh. Deut. Naturwiss. Med. Ver. Böhmen.</i> . . .          | Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen. |
| <i>Acta. Sci. Fennicae</i> . . .                              | Acta Societatis Scientiarum Fennicae.  |
| <i>Agric. Bull. F. M. S.</i> . . .                            | Agricultural Bulletin of the Federated Malay States.                                 |
| <i>Agric. J. India</i> . . .                                  | Agricultural Journal of India.   |
| <i>Agric. Res. Inst., Pusa Rep. (Gull.)</i> . . .             | Agricultural Research Institute, Pusa, Report and Bulletins.                         |
| <i>Allgem. Z. Bierbrau. u. Malzfabr.</i> . . .                | Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.                         |
| <i>Amer. J. Bot.</i> . . .                                    | American Journal of Botany.  |
| <i>Amer. J. Dis. Children</i> . . .                           | American Journal of Diseases of Children.  |
| <i>Amer. J. Pharm.</i> . . .                                  | American Journal of Pharmacy.  |
| <i>Amer. J. Physiol.</i> . . .                                | American Journal of Physiology.  |
| <i>Amer. J. Publ. Health</i> . . .                            | American Journal of Public Health.   |
| * <i>Amer. J. Sci.</i> . . .                                  | American Journal of Science.   |
| <i>Amer. Min.</i> . . .                                       | American Mineralogist.   |
| <i>Anal. Asoc. Quím. Argentina</i> . . .                      | Anales de la Asociación Química Argentina.   |
| <i>Anal. Fis. Quím.</i> . . .                                 | Anales de la Sociedad Española de Física y Química.                                  |
| * <i>Analyst</i> . . .  | Analyst.   |
| <i>Annalen</i> . . .  | Justus Liebig's Annalen der Chemie.  |
| <i>Ann. Bot.</i> . . .  | Annals of Botany.  |
| <i>Ann. di Bot.</i> . . .                                     | Annali di Botanica.  |
| <i>Ann. Chim.</i> . . .                                       | Annales de Chimie.   |
| * <i>Ann. Chim. Analyt.</i> . . .                             | Annales de Chimie Analytique et de Chimie Appliquées.                                |
| <i>Ann. di Chim. Appl.</i> . . .                              | Annali di Chimica Applicata.   |
| <i>Ann. Falsif.</i> . . .                                     | Annales des Falsifications.  |
| <i>Ann. hyg. pub. med. legale.</i> . . .                      | Annales d'hygiène publique et de médecine légale.                                    |
| <i>Ann. Inst. Pasteur</i> . . .                               | Annales de l'Institut Pasteur.   |
| <i>Ann. Physik</i> . . .                                      | Annalen der Physik.  |
| <i>Ann. Physique</i> . . .                                    | Annales de Physique.   |
| <i>Ann. R. Staz. Chim. Agrar. Sperim.</i> . . .               | Annali della R. Stazione Chimico Agraria Sperimen tale di Roma.                      |
| <i>Ann. sci. Univ. Jassy</i> . . .                            | Annales scientifiques de l'Université de Jassy.                                      |
| <i>Ann. Soc. Geol. Belg.: Publ. rel. au Congo Belge</i> . . . | Annales de la Société géologique de Belgique: Publications relatives au Congo Belge. |
| <i>Apoth. Zeit.</i> . . .                                     | Apotheker-Zeitung.   |
| <i>Arb. Gebiet. Physik, Math. Chem.</i> . . .                 | Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.                          |
| <i>Arch. Entw.-mech. Org.</i> . . .                           | Archiv für Entwicklungsmechanik der Organismen.                                      |
| <i>Arch. exp. Path. Pharm.</i> . . .                          | Archiv für experimentelle Pathologie und Pharmakologie.                              |
| <i>Arch. Farm. sperim. Sci. aff.</i> . . .                    | Archivio di Farmacologia sperimentale e Scienze affini.                              |

| ABBREVIATED TITLE.                                     | JOURNAL.   |
|--|--|
| <i>Arch. Fisiol.</i> . . .                             | Archivio di Fisiologia.  |
| <i>Arch. Int. Med.</i> . . .                           | The Archives of Internal Medicine.   |
| <i>Arch. Ital. Biol.</i> . . .                         | Archives italiennes de Biologie.   |
| <i>Arch. Med. Pharm. milit.</i> . . .                  | Archives de Médecine et de Pharmacie militaires.   |
| <i>Arch. Néerland.</i> . . .                           | Archives Néerlandaises de sciences exactes et naturelles.                                  |
| <i>Arch. Néerland. physiol.</i> . . .                  | Archives Néerlandaises de physiologie de l'homme et des animaux.                           |
| * <i>Arch. Pharm.</i> . . .                            | Archiv der Pharmazie.  |
| <i>Arch. Sci. phys. nat.</i> . . .                     | Archives des Sciences physiques et naturelles.   |
| <i>Arch. Suikerind. Ned. Indie</i> . . .               | Archief voor de Suikerindustrie in Nederlandach-<br>Indië.                                 |
| <i>Arkiv Kem. Min. Geol.</i> . . .                     | Arkiv för Kemi, Mineralogi och Geologi.  |
| <i>Astrophys. J.</i> . . .                             | Astrophysical Journal.   |
| * <i>Atti R. Accad. Lincei</i> . . .                   | Atti della Reale Accademia Nazionale dei Lincei.   |
| <i>Atti R. Accad. Sci. Torino</i> . . .                | Atti della Reale Accademia delle Scienze di Torino.  |
| <i>Atti R. Ist. Veneto Sci.</i> . . .                  | Atti del Reale Istituto Veneto di Scienze, Lettere ed<br>Arti.                             |
| <i>Aust. Pharm. Notes</i> . . .                        | Australian Pharmaceutical Notes and News.  |
| <i>Beitr. Min. Japan</i> . . .                         | Beiträge zur Mineralogie von Japan.  |
| <i>Berg. Hüttenm. Rundsch.</i> . . .                   | Berg- und Hüttenmannisches Rundschau.  |
| * <i>Ber.</i> . . .                                    | Berichte der Deutschen chemischen Gesellschaft.  |
| <i>Ber. Deut. bot. Ges.</i> . . .                      | Berichte der Deutschen botanischen Gesellschaft.   |
| * <i>Ber. Deut. pharm. Ges.</i> . . .                  | Berichte der Deutschen pharmazeutischen Gesellschaft.                                      |
| <i>Ber. Oberhess. Ges. Natur-<br/>Heilkunde.</i> . . . | Berichte der Oberhessischen Gesellschaft für Natur-<br>und Heilkunde zu Giessen.           |
| <i>Ber. Ohara Inst. landw.<br/>Forsch.</i> . . .       | Berichte des Ohara Instituts für landwirtschaftliche<br>Forschungen.                       |
| <i>Ber. Sächs. Akad. Wiss.</i> . . .                   | Berichte über die Verhandlungen der Sächsischen<br>Akademie der Wissenschaften zu Leipzig. |
| <i>Berlin. Klin. Woch.</i> . . .                       | Berliner Klinische Wochenschrift.  |
| * <i>Bied. Zentr.</i> . . .                            | Biedermann's Zentralblatt.   |
| * <i>Biochem. J.</i> . . .                             | Biochemical Journal.   |
| * <i>Biochem. Z.</i> . . .                             | Biochemische Zeitschrift.  |
| <i>Bd. of Trade J.</i> . . .                           | Board of Trade Journal.  |
| <i>Bol. Acad. Nac. Ciencias,<br/>Cordoba.</i> . . .    | Boletín de la Academia Nacional de Ciencias, Córdoba.                                      |
| * <i>Boll. Chim. farm.</i> . . .                       | Bollettino Chimico farmaceutico.   |
| <i>Boll. Soc. Geol. Ital.</i> . . .                    | Bollettino della Società Geologica Italiana.   |
| <i>Boll. Soc. Med. Chirurg.</i> . . .                  | Bollettino della Società Medico-Chirurgica, Pavia  |
| <i>Bot. Centr.</i> . . .                               | Botanisches Centralblatt.  |
| <i>Bot. Gaz.</i> . . .                                 | Botanical Gazette.   |
| <i>Brass. Malt.</i> . . .                              | Brasserie et Malterie.   |
| <i>Brau- u. Malzind.</i> . . .                         | Brau- u. Malzindustrie.  |
| <i>Braunkohle</i> . . .                                | Braunkohle.  |
| * <i>Brennstoff-Chem.</i> . . .                        | Brennstoff-Chemie.   |
| <i>Brewers' J.</i> . . .                               | Brewers' Journal.  |
| <i>Brit. J. Phot.</i> . . .                            | British Journal of Photography.  |
| <i>Brit. Med. J.</i> . . .                             | British Medical Journal.   |
| <i>Brit. Pat.</i> . . .                                | British Patent.  |
| <i>Buletinul Chim.</i> . . .                           | Buletinul Chimie.  |
| <i>Bul. Soc. Chim. România</i> . . .                   | Buletinul Societății de Chimie din România.  |
| <i>Bul. Soc. Romane Stiin.</i> . . .                   | Buletinul Societății Române de Științe.  |
| <i>Bull. Acad. roy. Belg.</i> . . .                    | Académie royale de Belgique—Bulletin de la Classe<br>des Sciences.                         |
| <i>Bull. Acad. Sci. Roumaine</i> . . .                 | Bulletin de la Section Scientifique de l'Académie<br>Roumaine.                             |
| <i>Bull. Assoc. Chim. Sucri.</i> . . .                 | Bulletin de l'Association des Chimistes de Sucrierie et<br>de Distillerie.                 |

| ABBREVIATED TITLE.                           | JOURNAL.   |
|--|--|
| Bull. Bureau of Standards (U.S.A.).          | Bulletin of the Bureau of Standards (U.S.A.).  |
| Bull. Com. Géol. Finlande.                   | Bulletin de la Commission Géologique de Finlande.  |
| Bull. Forest Exp. Stat. Meguro.              | Bulletin of the Forest Experiment Station, Meguro, Tokyo.                                      |
| Bull. gén. Thérap.                           | Bulletin général de Thérapentique médicale, chirurgicale, obstétricale.                        |
| Bull. Geol. d'Alsace.                        | Bulletin du Service de la Carte Géologique d'Alsace et de Lorraine.                            |
| Bull. Geol. Inst. Univ. Upsala.              | Bulletin of the Geological Institution of the University of Upsala.                            |
| Bull. Geol. Soc. Amer.                       | Bulletin of the Geological Society of America.   |
| Bull. Geol. Survey, U.S.A.                   | Bulletin of the U.S. Geological Survey.  |
| Bull. Geol. Survey, West Australia.          | Bulletin of the Geological Survey, West Australia.   |
| Bull. Imp. Inst.                             | Bulletin of the Imperial Institute.  |
| Bull. Indian Ind. Lab.                       | Bulletin of Indian Industries and Labour.  |
| Bull. Inst. Phys. Chem. Res., Japan.         | Bulletin of the Institute of Physical and Chemical Research, Japan (Rikwagakun Kerkynjo Ihô).  |
| Bull. Johns Hopkins Hospital.                | Bulletin of the Johns Hopkins Hospital.  |
| Bull. School Mines and Met., Univ. Missouri. | Bulletin of the School of Mines and Metallurgy, University of Missouri.                        |
| Bull. Sci. Pharmacol.                        | Bulletin des Sciences Pharmacologiques.  |
| *Bull. Soc. chim.                            | Bulletin de la Société chimique de France.   |
| *Bull. Soc. chim. Belg.                      | Bulletin de la Société chimique de Belgique.   |
| Bull. Soc. Chim. biol.                       | Bulletin de la Société de Chimie biologique.   |
| Bull. Soc. d'Encour.                         | Bulletin de la Société d'Encouragement pour l'Industrie Nationale.                             |
| Bull. Soc. franç. Min.                       | Bulletin de la Société française de Minéralogie.   |
| Bull. Soc. Franç. Phot.                      | Bulletin de la Société Française de Photographie.  |
| Bull. Soc. Géol. Belg.                       | Bulletin de la Société Géologique de Belgique.   |
| Bull. Soc. Ind. Mulhouse.                    | Bulletin de la Société Industrielle de Mulhouse.   |
| Bull. Soc. Ind. Nord.                        | Bulletin de la Société Industrielle du Nord de la France.                                      |
| Bull. Soc. Oural. Sci. Nat.                  | Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.        |
| Bull. Soc. Pharm. Bordeaux.                  | Bulletin des Travaux de la Société de Pharmacie de Bordeaux.                                   |
| Bull. Wellcome Trop. Res. Lab.               | Bulletin of the Wellcome Tropical Research Laboratory.   |
| Cairo Sci. J.                                | Cairo Scientific Journal.  |
| Canada Dept. Mines Publ.                     | Canada Department of Mines Publications.   |
| *Canadian Chem. Met.                         | Canadian Chemistry and Metallurgy.   |
| Canadian Med. Assoc. J.                      | Canadian Medical Association Journal.  |
| Caoutchouc et Gutta-Percha.                  | Le Caoutchouc et le Gutta-Percha.  |
| Časopis. Math. Fysiky                        | Casopis pro přetování Matematické a Fysiky.  |
| Cellulosechem.                               | Cellulosechemie.   |
| Centr. Min.                                  | Centralblatt für Mineralogie, Geologie und Paläontologie.                                      |
| Ch. of Comm. J.                              | Chamber of Commerce Journal.   |
| Chem. App.                                   | Chemische Apparatur.   |
| Chem. Erde                                   | Chemie der Erde.   |
| Chem. Ind.                                   | Chemische Industrie.   |
| Chem. Listy                                  | Chemické Listy pro Vědu a Průmysl. Organ de la "Česká chemická Společnost pro Vědu a Průmysl." |
| *Chem. and Met. Eng.                         | Chemical and Metallurgical Engineering.  |
| *Chem. News                                  | Chemical News.   |

| ABBREVIATED TITLE.                            | JOURNAL.  |
|---|---|
| Chem. Trade J. . . . .                        | Chemical Trade Journal.   |
| Chem. Umschau . . . . .                       | Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.     |
| *Chem. Weekblad . . . . .                     | Chemisch Weekblad.  |
| *Chem. Ztg. . . . .                           | Chemiker-Zeitung.   |
| *Chem. Zentr. . . . .                         | Chemisches Zentralblatt.  |
| Chem. and Drug. . . . .                       | Chemist and Druggist.   |
| *Chim. et Ind. . . . .                        | Chimie et Industrie.  |
| Collegium . . . . .                           | Collegium.  |
| *Compt. rend. . . . .                         | Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.      |
| Compt. rend. Soc. Biol. . . . .               | Comptes rendus hebdomadaires de Séances de la Société de Biologie.        |
| Comptes rend. Trav. Lab. Carlsberg . . . . .  | Comptes rendus des Travaux du Laboratoire Carlsberg.                      |
| D. R. P. . . . .                              | Deutsches Reichs-Patent.  |
| Dept. Chem. S. Australia, Bull. . . . .       | Department of Chemistry, South Australia, Bulletins.                      |
| Deut. med. Woch. . . . .                      | Deutsche medizinische Wochenschrift.                                      |
| Econ. Geol. . . . .                           | Economic Geology.   |
| Econ. Proc. Roy. Dubl. Soc. . . . .           | Economic Proceedings of the Royal Dublin Society.                         |
| Engineering . . . . .                         | Engineering.  |
| Eng. and Min. J. . . . .                      | Engineering and Mining Journal.   |
| Exper. Stat. Rec. . . . .                     | Experiment Station Record.  |
| Farben-Ztg. . . . .                           | Farben-Zeitung.   |
| Fermentforsch. . . . .                        | Fermentforschung.   |
| Feuerungstechnik . . . . .                    | Feuerungstechnik.   |
| Flora . . . . .                               | Flora.  |
| Földtani Közlem. . . . .                      | Földtani Közlem.  |
| Fr. Pat. . . . .                              | French Patent.  |
| Gas J. . . . .                                | Gas Journal.  |
| Gas World . . . . .                           | Gas World.  |
| *Gazzetta . . . . .                           | Gazzetta chimica italiana.  |
| Geol. För. Förh. . . . .                      | Geologiska Föreningens i Stockholm Förhandlingar.                         |
| Geol. Mag. . . . .                            | Geological Magazine.  |
| Gerber . . . . .                              | Gerber.   |
| *Giorn. Chim. Ind. Appl. . . . .              | Giornale di Chimica Industriale ed Applicata.                             |
| Gummi-Ztg. . . . .                            | Gummi-Zeitung.  |
| Handl. Vijft. Nat. . . . .                    | Handelingen van het Vijftende Natuur.                                     |
| Hawaii Agric. Exp. Stat. Bull. . . . .        | Hawaii Agricultural Experiment Station Bulletins.                         |
| Heart . . . . .                               | Heart.  |
| Helv. Chim. Acta. . . . .                     | Helvetica Chimica Acta.   |
| Indian J. Med. Res. . . . .                   | Indian Journal of Medical Research.                                       |
| India-rubber J. . . . .                       | India-rubber Journal.   |
| *Ind. Eng. Chem. . . . .                      | Industrial and Engineering Chemistry.                                     |
| Int. Rev. Sci. Pract. Agric. . . . .          | International Review of the Science and Practice of Agriculture.          |
| Int. Sugar J. . . . .                         | International Sugar Journal.  |
| Iron Steel Inst. Carnegie Schol. Mem. . . . . | Iron and Steel Institute, Carnegie Scholarship Memoirs.                   |
| Jahrb. Geol. Reichsanst. . . . .              | Jahrbuch der geologischen Reichsanstalt.                                  |
| Jahrb. Min. . . . .                           | Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.               |
| Jahrb. Min. Beil.-Bd. . . . .                 | Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band. |
| Jahrb. Radioaktiv. Elektr. . . . .            | Jahrbuch der Radioaktivität und Elektronik.                               |
| Jahrb. wiss. Bot. . . . .                     | Jahrbuch für wissenschaftliche Botanik.                                   |

| ABBREVIATED TITLE.                     | JOURNAL.   |
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| <i>Jahresber. Ges. vaterl. Kultur.</i> | <i>Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.</i>      |
| <i>Japan. J. Phys.</i>                 | <i>Japanese Journal of Physics.</i>  |
| <i>Jernk. Ann.</i>                     | <i>Jern-kontorsts Annaler.</i>   |
| <i>*J. Agric. Res.</i>                 | <i>Journal of Agricultural Research.</i>   |
| <i>*J. Agric. Sci.</i>                 | <i>Journal of Agricultural Science.</i>  |
| <i>J. Amer. Ceram. Soc.</i>            | <i>Journal of the American Ceramic Society.</i>                                    |
| <i>*J. Amer. Chem. Soc.</i>            | <i>Journal of the American Chemical Society.</i>                                   |
| <i>J. Amer. Leather Assoc.</i>         | <i>Journal of the American Leather Chemists' Association.</i>                      |
| <i>J. Amer. Med. Assoc.</i>            | <i>Journal of the American Medical Association.</i>                                |
| <i>J. Assoc. Off. Agric. Chem.</i>     | <i>Journal of the Association of Official Agricultural Chemists.</i>               |
| <i>*J. Biol. Chem.</i>                 | <i>Journal of Biological Chemistry.</i>  |
| <i>J. Canad. Min. Inst.</i>            | <i>Journal of the Canadian Mining Institute.</i>                                   |
| <i>J. Chem. Ind. Tokyo</i>             | <i>See Kōgyō-Kwagaku-Zasshi.</i>   |
| <i>J. Chem. Met. Soc. S. Africa</i>    | <i>Journal of the Chemical, Metallurgical, and Mining Society of South Africa.</i> |
| <i>J. Chem. Soc. Japan.</i>            | <i>Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)</i>        |
| <i>J. Chim. physique</i>               | <i>Journal de Chimie physique.</i>   |
| <i>J. Coll. Agric. Hokkaido</i>        | <i>Journal of the College of Agriculture, Hokkaidō Imperial University, Japan.</i> |
| <i>J. Coll. Agric. Tokyo</i>           | <i>Journal of the College of Agriculture, Imperial University of Tokyo, Japan.</i> |
| <i>J. Coll. Eng. Tokyo</i>             | <i>Journal of the College of Engineering, Imperial University of Tokyo.</i>        |
| <i>*J. Coll. Sci. Tokyo</i>            | <i>Journal of the College of Science, Imperial University of Tokyo.</i>            |
| <i>J. Exp. Med.</i>                    | <i>Journal of Experimental Medicine.</i>   |
| <i>*J. Franklin Inst.</i>              | <i>Journal of the Franklin Institute.</i>  |
| <i>J. Gasbeleucht.</i>                 | <i>Journal für Gasbeleuchtung und Wasserversorgung.</i>                            |
| <i>J. gen. Physiol.</i>                | <i>Journal of general Physiology.</i>  |
| <i>J. Genetics</i>                     | <i>Journal of Genetics.</i>  |
| <i>J. Geol.</i>                        | <i>Journal of Geology.</i>   |
| <i>J. Geol. Soc. Tokyo</i>             | <i>Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).</i>          |
| <i>J. Hygiene</i>                      | <i>Journal of Hygiene.</i>   |
| <i>J. Indian Ind. Lab.</i>             | <i>Journal of Indian Industries and Labour.</i>                                    |
| <i>*J. Indian Inst. Sci.</i>           | <i>Journal of the Indian Institute of Science.</i>                                 |
| <i>J. Inst. Brewing</i>                | <i>Journal of the Institute of Brewing.</i>  |
| <i>J. Inst. Metals</i>                 | <i>Journal of the Institute of Metals.</i>   |
| <i>J. Inst. Petroleum Tech.</i>        | <i>Journal of the Institution of Petroleum Technologists.</i>                      |
| <i>J. Iron and Steel Inst.</i>         | <i>Journal of the Iron and Steel Institute.</i>                                    |
| <i>J. Landw.</i>                       | <i>Journal für Landwirtschaft.</i>   |
| <i>J. Marine Biol. Assoc. U.K.</i>     | <i>Journal of the Marine Biological Association of the United Kingdom.</i>         |
| <i>J. Med. Res.</i>                    | <i>Journal of Medical Research.</i>  |
| <i>J. Min. Agric.</i>                  | <i>Journal of the Ministry of Agriculture.</i>                                     |
| <i>J. Path. Bact.</i>                  | <i>Journal of Pathology and Bacteriology.</i>                                      |
| <i>J. Opt. Soc. Amer.</i>              | <i>Journal of the Optical Society of America.</i>                                  |
| <i>*J. Pharm. Chim.</i>                | <i>Journal de Pharmacie et de Chimie.</i>  |
| <i>J. Pharm. Expt. Ther.</i>           | <i>Journal of Pharmacology and Experimental Therapeutics.</i>                      |
| <i>J. Pharm. Soc. Japan</i>            | <i>Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).</i>            |
| <i>*J. Physical Chem.</i>              | <i>Journal of Physical Chemistry.</i>  |
| <i>J. Physiol.</i>                     | <i>Journal of Physiology.</i>  |

| ABBREVIATED TITLE.                                 | JOURNAL.  |
|--|---|
| <i>J. Physiol. Path. gén.</i> . . .                | <i>Journal de Physiologie et de Pathologie générale.</i>                |
| <i>J. Phys. Radium</i> . . .                       | <i>Journal de Physique et le Radium.</i>                                |
| * <i>J. pr. Chem.</i> . . .                        | <i>Journal für praktische Chemie.</i>                                   |
| <i>J. Proc. Asiatic Soc. Bengal.</i>               | <i>Journal and Proceedings of the Asiatic Society of Bengal.</i>        |
| <i>J. Proc. Roy. Soc. New South Wales.</i>         | <i>Journal and Proceedings of the Royal Society of New South Wales.</i> |
| <i>J. Roy. Agric. Soc.</i> . . .                   | <i>Journal of the Royal Agricultural Society.</i>                       |
| <i>J. Roy. Army Med. Corps</i> . . .               | <i>Journal of the Royal Army Medical Corps.</i>                         |
| <i>J. Roy. Hort. Soc.</i> . . .                    | <i>Journal of the Royal Horticultural Society.</i>                      |
| <i>J. Roy. Soc. New South Wales.</i>               | <i>Journal and Proceedings of the Royal Society of New South Wales.</i> |
| <i>J. Roy. Soc. West Australia</i>                 | <i>Journal of the Royal Society of West Australia.</i>                  |
| * <i>J. Russ. Phys. Chem. Soc.</i>                 | <i>Journal of the Physical and Chemical Society of Russia.</i>          |
| <i>J. Scot. Md. Soc.</i> . . .                     | <i>Journal of the Scottish Meteorological Society.</i>                  |
| <i>J. Soc. Arts</i> . . .                          | <i>Journal of the Royal Society of Arts.</i>                            |
| <i>J. Soc. Dyers and Col.</i> . . .                | <i>Journal of the Society of Dyers and Colourists.</i>                  |
| <i>J. Soc. Leather Trades Chem.</i>                | <i>Journal of the Society of Leather Trades Chemists.</i>               |
| <i>J. Soc. Glass Technology</i> . . .              | <i>Journal of the Society of Glass Technology.</i>                      |
| [ <i>J. S. African Assoc. Anal. Chem.</i> ]        | <i>Journal of the South African Association of Analytical Chemists.</i> |
| <i>Changed 1922 to</i>                             |   |
| <i>J. S. African Chem. Inst.</i> . . .             | <i>Journal of the South African Chemical Institute.</i>                 |
| <i>J. Textile Inst.</i> . . .                      | <i>Journal of the Textile Institute.</i>                                |
| <i>J. Usines Gaz</i> . . .                         | <i>Journal des Usines à Gaz.</i>  |
| <i>J. Washington Acad. Sci.</i> . . .              | <i>Journal of the Washington Academy of Science.</i>                    |
| <i>J. West Scotland Iron Steel Inst.</i>           | <i>Journal of the West of Scotland Iron and Steel Institute.</i>        |
| <i>K. Svenska Vet. Akad. Handl.</i>                | <i>Kongliga Svenska Vetenskaps Akademiens Handlingar.</i>               |
| <i>Kentucky Exp. Stat. Bull.</i>                   | <i>Kentucky Experimental Station, Bulletin.</i>                         |
| <i>Keram. Rundsch.</i> . . .                       | <i>Keramisch Rundschau.</i>   |
| <i>Kew Bull.</i> . . .                             | <i>Kew Bulletin.</i>  |
| <i>Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).</i> | <i>Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).</i>      |
| * <i>Kolloid Z.</i> . . .                          | <i>Kolloid Zeitschrift.</i>   |
| * <i>Koll. Chem. Beihefte</i> . . .                | <i>Kolloid-chemische Beihefte.</i>                                      |
| <i>Kosmos</i> . . .                                | <i>Kosmos (Lemberg).</i>  |
| <i>Kühn-Archiv</i> . . .                           | <i>Kühn-Archiv.</i>   |
| <i>Kunststoffe</i> . . .                           | <i>Kunststoffe.</i>   |
| <i>Lancet</i> . . .                                | <i>The Lancet.</i>  |
| <i>Landw. Jahrb.</i> . . .                         | <i>Landwirtschaftliche Jahrbücher.</i>                                  |
| <i>Landw. Versuchs-Stat.</i> . . .                 | <i>Die landwirtschaftlichen Versuchs Stationen.</i>                     |
| <i>Leather Trades Rev.</i> . . .                   | <i>Leather Trades Review.</i>   |
| <i>Louisiana Bull.</i> . . .                       | <i>Louisiana Bulletin.</i>  |
| <i>Louisiana Planter</i> . . .                     | <i>Louisiana Planter.</i>   |
| <i>Lunds Univ. Arskr.</i> . . .                    | <i>Lunds Universitets Årskrift.</i>                                     |
| <i>Math. et Termes. Ért.</i> . . .                 | <i>Mathematikai és Természettudományi Értesítő, Budapest.</i>           |
| <i>Medd. K. Vetenskapskad. Nobel-Inst.</i>         | <i>Meddelanden från Kongl. Vetenskapsakademiens Nobel-Institut.</i>     |
| <i>Medd. on Grönland</i> . . .                     | <i>Meddelelser on Grönland.</i>   |
| <i>Med. Genes. Lab. Weltevreden.</i>               | <i>Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden.</i>  |
| <i>Med. Chron.</i> . . .                           | <i>Medical Chronicle.</i>   |
| <i>Med. Klinik</i> . . .                           | <i>Medizinische Klinik.</i>   |
| <i>Mem. Acad. Lincei</i> . . .                     | <i>Memorie della Reale Accademia dei Lincei.</i>                        |
| <i>Mem. Acad. Sci. Torino</i> . . .                | <i>Memorie della Reale Accademia delle Scienze di Torino.</i>           |

| ABBREVIATED TITLE.                                    | JOURNAL.   |
|---|--|
| <i>Mem. Coll. Sci. Kyôto</i>                          | Memoirs of the College of Science, Kyôto Imperial University.                                |
| <i>Mem. Coll. Sci. and Eng. Kyôto Imp. Univ.</i>      | Memoirs of the College of Science and Engineering, Kyôto Imperial University.                |
| <i>Mem. Dept. Agric. India</i>                        | Memoirs of the Department of Agriculture in India.   |
| <i>Mem. Manchester Phil. Soc.</i>                     | Memoirs and Proceedings of the Manchester Literary and Philosophical Society.                |
| <i>Mem. Soc. Ing. Civ.</i>                            | Mémoires de la Société des Ingénieurs Civils de France.                                      |
| <i>Mem. Soc. Toscana Sci. Nat.</i>                    | Memorie della Società Toscana di Scienze naturali residente in Pisa.                         |
| <i>Mém. Poudres</i>                                   | Mémorial des Poudres.  |
| <i>Metall u. Erz</i>                                  | Metall und Erz.  |
| <i>Metrop. Water Bd. Rep.</i>                         | Metropolitan Water Board Reports.  |
| <i>Milch. Zentr.</i>                                  | Milchwirtschaftliches Zentralblatt.  |
| <i>Min. Mag.</i>                                      | Mineralogical Magazine and Journal of the Mineralogical Society.                             |
| <i>Mitt. Materialprüf.</i>                            | Mittheilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.                        |
| <i>Mitt. med. Ges. Tokyo</i>                          | Mittheilungen der medizinischen Gesellschaft zu Tokyo.                                       |
| <i>Mitt. Naturforsch. Ges. Halle.</i>                 | Mittheilungen der Naturforschenden Gesellschaft zu Halle.                                    |
| <i>Mitt. Path. Inst. K. Univ. Japan.</i>              | Mittheilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan. |
| <i>*Monatsh.</i>                                      | Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.                           |
| <i>Monatsh. Math. Physik</i>                          | Monatshefte für Mathematik und Physik.   |
| <i>*Mon. Sci.</i>                                     | Moniteur Scientifique.   |
| <i>Month. Not. Roy. Astr. Soc.</i>                    | Monthly Notices of the Royal Astronomical Society, London.                                   |
| <i>Münch. med. Woch.</i>                              | Münchener medizinische Wochenschrift.  |
| <i>Nachr. G.s. Wiss. Göttingen.</i>                   | Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.                            |
| <i>Nature</i>   | Nature.  |
| <i>Naturwiss.</i>                                     | Die Naturwissenschaften.   |
| <i>Naturw. Rdsch.</i>                                 | Naturwissenschaftliche Rundschau.  |
| <i>New York Agr. Expt. Sta. Bull.</i>                 | New York Agricultural Experiment Station Bulletins.  |
| <i>New Zealand Dominion Laby. Rept.</i>               | New Zealand Dominion Laboratory Reports.   |
| <i>New Zealand Jnl. of Science and Technology</i>     | New Zealand Journal of Science and Technology.   |
| <i>Nippon Kwagaku Kwaï Shi (J. Chem. Soc. Japan).</i> | Nippon Kwagaku Kwa Shi (Journal of the Chemical Society of Japan).                           |
| <i>Nova Acta Soc. Sci.</i>                            | Nova Acta Regiæ Societatis Scientiarum Upsaliensis.  |
| <i>Nuovo Cim.</i>                                     | Il Nuovo Cimento.  |
| <i>Öfvers. Finska Vet.-Soc.</i>                       | Öfversigt af Finska Vetenskaps-Societätens Förhandlingar, Helsingfors.                       |
| <i>*Oesterr. Chem.-Zeit.</i>                          | Oesterreichische Chemiker-Zeitung.   |
| <i>Oil and Colour Trades J.</i>                       | Oil and Colour Trades Journal.   |
| <i>Oil, Paint, and Drug Rep.</i>                      | Oil, Paint, and Drug Reporter.   |
| <i>Oversigt Danske Vid. selsk.</i>                    | Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.                    |
| <i>Paper</i>  | Paper.   |
| <i>Papierfabr.</i>                                    | Papier-Fabrikant.  |
| <i>Perf. and Essent. Oil Rec.</i>                     | Perfumery and Essential Oil Record.  |
| <i>Per. spis. Sofia</i>                               | Periodicesko spisanie Sofia.   |
| <i>Petroleum Age.</i>                                 | Petroleum Age, including Petroleum.  |

| ABBREVIATED TITLE.                           | JOURNAL.  |
|--|---|
| <i>Pfûger's Archiv</i> . . .                 | Archiv für die gesamte Physiologie des Menschen und der Thiere.                     |
| Pharm. J. . . . .                            | Pharmaceutical Journal.   |
| *Pharm. Weekblad . . .                       | Pharmaceutisch Weekblad.  |
| *Pharm. Zentr.-h. . . .                      | Pharmazeutische Zentrallhalle.  |
| Phil. Mag. . . . .                           | Philosophical Magazine (The London, Edinburgh and Dublin).                          |
| Phil. Trans. . . . .                         | Philosophical Transactions of the Royal Society of London.                          |
| Philippine J. Sci. . . .                     | Philippine Journal of Science.  |
| Phot. J. . . . .                             | Photographic Journal.   |
| Phot. Korr. . . . .                          | Photographische Korrespondenz.  |
| Physical Rev. . . . .                        | Physical Review.  |
| Physikal. Z. . . . .                         | Physikalische Zeitschrift.  |
| Proc. Amer. Phil. Soc. . .                   | Proceedings of the American Philosophical Society.                                  |
| Proc. Amer. Physiol. Soc. .                  | Proceedings of the American Physiological Society.                                  |
| *Proc. Amer. Soc. Biol. Chem. . . . .        | Proceedings of the American Society of Biological Chemists.                         |
| Proc. Amer. Soc. Civ. Eng. .                 | Proceedings of the American Society of Civil Engineers.                             |
| Proc. Amer. Soc. Testing Materials . . . .   | Proceedings of American Society for Testing Materials.                              |
| Proc. Austral. Inst. Min. Met. . . . .       | Proceedings of the Australasian Institute of Mining and Metallurgy.                 |
| Proc. Camb. Phil. Soc. . .                   | Proceedings of the Cambridge Philosophical Society.                                 |
| Proc. Durham Phil. Soc. . .                  | Proceedings of the Durham Philosophical Society.                                    |
| Proc. Eng. Soc. W. Pa. . .                   | Proceedings of the Engineers' Society of Western Pennsylvania.                      |
| Proc. Inst. Civ. Eng. . . .                  | Proceedings of the Institution of Civil Engineers.                                  |
| Proc. Inst. Mech. Eng. . .                   | Proceedings of the Institution of Mechanical Engineers.                             |
| *Proc. K. Akad. Wetensch. Amsterdam. . . . . | Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version). |
| Proc. Nat. Acad. Sci. . .                    | Proceedings of the National Academy of Sciences.                                    |
| Proc. Nova Scotia Inst. Sci. . . . .         | Proceedings of the Nova Scotia Institute of Science.                                |
| Proc. Phil. Soc. Glasgow . .                 | Proceedings of the Glasgow Philosophical Society.                                   |
| Proc. Physical Soc. . . .                    | Proceedings of the Physical Society of London.                                      |
| Proc. Physiol. Soc. . . .                    | Proceedings of the Physiological Society.   |
| Proc. Roy. Inst. . . . .                     | Proceedings of the Royal Institution of Great Britain.                              |
| Proc. Roy. Irish Acad. . .                   | Proceedings of the Royal Irish Academy.   |
| *Proc. Roy. Soc. . . . .                     | Proceedings of the Royal Society.   |
| Proc. Roy. Soc. Edin. . . .                  | Proceedings of the Royal Society of Edinburgh.                                      |
| Proc. Roy. Soc. Med. . . .                   | Proceedings of the Royal Society of Medicine.                                       |
| Proc. Roy. Soc. Queensland .                 | Proceedings of the Royal Society of Queensland.                                     |
| Proc. Roy. Soc. Tasmania . .                 | Proceedings of the Royal Society of Tasmania.                                       |
| Proc. Sci. Assoc., Vizianagram . . . . .     | Proceedings of the Science Association, Maharajah's College, Vizianagram.           |
| Proc. Soc. Exp. Biol. Med. .                 | Proceedings of the Society for Experimental Biology and Medicine.                   |
| Proc. U.S. Nat. Mus. . . .                   | Proceedings of the United States National Museum.                                   |
| Proc. verb. Soc. Toscana Sci. Nat. . . . .   | Processi verbali Società Toscana di Scienze Naturali.                               |
| Pulp and Paper Magazine . .                  | Pulp and Paper Magazine of Canada.  |
| Quart. J. Geol. Soc. . . .                   | Quarterly Journal of the Geological Society.  |
| Quart. J. Med. . . . .                       | Quarterly Journal of Medicine.  |
| Radium in Biol. Heilkunde .                  | Radium in Biologie und Heilkunde.   |
| Rec. Australian Mus. . . .                   | Records of the Australian Museum.   |
| Rec. trav. bot. Néerland. . .                | Recueil des travaux botaniques Néerlandaises.                                       |
| *Rec. trav. chim. . . . .                    | Recueil des travaux chimiques des Pays-Bas.   |

| ABBREVIATED TITLE.                      | JOURNAL.  |
|---|---|
| Wiss. Veröff. Siemens Konz.             | Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.                 |
| Wochbl. Papierfabr. . .                 | Wochenblatt für Papierfabrikation.  |
| Woch. f. Brau. . .                      | Wochenschrift für Brauerei.   |
| *Yakugakuzasshi (J. Pharm. Soc. Japan). | Yakugakuzasshi (Journal of the Pharmaceutical Society of Japan).              |
| Z. allg. Physiol. . .                   | Zeitschrift für allgemeine Physiologie.                                       |
| *Z. anal. Chem. . .                     | Zeitschrift für analytische Chemie.   |
| *Z. angew. Chem. . .                    | Zeitschrift für angewandte Chemie.  |
| *Z. anorg. Chem. . .                    | Zeitschrift für anorganische und allgemeine Chemie.                           |
| Z. Biol. . .                            | Zeitschrift für Biologie.   |
| Z. deut. Geol. Ges. . .                 | Zeitschrift der deutschen Geologischen Gesellschaft.                          |
| Z. deut. Oel-Fett Ind. . .              | Zeitschrift der deutschen Oel- und Fett-Industrie.                            |
| *Z. Elektrochem. . .                    | Zeitschrift für Elektrochemie.  |
| Z. exp. Path. Ther. . .                 | Zeitschrift für experimentelle Pathologie und Therapie.                       |
| Z. ges. Brauw. . .                      | Zeitschrift für das gesamte Brauwesen.  |
| Z. ges. exp. Med. . .                   | Zeitschrift für die gesamte experimentelle Medizin.                           |
| Z. ges. Schiess- u. Sprengstoffw. . .   | Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.                    |
| Z. Hyg. . .                             | Zeitschrift für Hygiene und Infektionskrankheiten.                            |
| Z. Immunit. . .                         | Zeitschrift für Immunitätsforschung und experimentelle Therapie.              |
| Z. Instrument. . .                      | Zeitschrift für Instrumentenkunde.  |
| Be Kryst. . .                           | Zeitschrift für Krystallographie.   |
| Z. Leder. Gerb. Chem. . .               | Zeitschrift für Leder- und Gerberei-Chemie.                                   |
| Z. öffentl. Chem. . .                   | Zeitschrift für öffentliche Chemie.   |
| Z. Physik. . .                          | Zeitschrift für Physik.   |
| *Z. physikal. Chem. . .                 | Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre. |
| Z. physikal. Chem. Unterr. . .          | Zeitschrift für den physikalischen und Chemischen Unterricht.                 |
| Z. physiol. Chem. . .                   | Hoppe-Seyler's Zeitschrift für physiologische Chemie.                         |
| Z. prakt. Geol. . .                     | Zeitschrift für praktische Geologie.  |
| *Z. Sauerstoff Stickstoff Ind. . .      | Zeitschrift für Sauerstoff und Stickstoff Industrie.                          |
| Z. Spiritusind. . .                     | Zeitschrift für Spiritusindustrie.  |
| Z. Unters. Nahr. Genussm. . .           | Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.                  |
| Z. Ver. deut. Zuckerind. . .            | Zeitschrift des Vereins der deutschen Zucker-Industrie.                       |
| Z. wiss. Mikrost. . .                   | Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.     |
| *Z. wiss. Photochem. . .                | Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie. |
| *Z. Zuckerind. Čechoslov. . .           | Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.               |
| *Zentr. Bakt. Par. . .                  | Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.     |
| Zentr. Zuckerind. . .                   | Zentralblatt für Zuckerindustrie.   |

JOURNAL  
OF  
THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

PART I.

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Organic Chemistry.

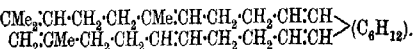
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**Composition of Paraffin Wax.** III. FRANCIS FRANCIS, CYRIL MERCER WATKINS, and REGINALD WILFRED WALLINGTON (T., 1922, 121, 2804—2810).

**Constitution of Squalene.** RIKÔ MAKIMA and BENNOSUKÉ KUBOTA (*Sci. Papers Inst. Phys. Chem. Research*, 1922, 1, 7—21).—Squalene,  $C_{30}H_{50}$ , is a highly unsaturated hydrocarbon isolated from shark's liver oil by Tsujimoto (*J. Chem. Ind. Japan*, 1906, 9, 958; 1917, 20, 953, 1069; A., 1916, i, 786; 1918, i, 89) and may be identical with Chapman's spinacene (T., 1917, 111, 56). The material used was the oil from the liver of *Squalus Mitsukurii*, and had b. p. 284—285°/25 mm.,  $d_4^{20}$  0.8596,  $n_D^{20}$  1.4959. When treated in chloroform solution with oxygen containing 5—7% of ozone, squalene hexaozonide,  $C_{30}H_{50}(O_3)_6$ , was obtained, which suffered decomposition when boiled with water; the products obtained from the ozonide prepared from 27 g. of squalene were as follows: carbon dioxide 1.82 g., formaldehyde undetermined, acetone 1.01 g., acetone peroxide 0.7 g., lævulinaldehyde 0.84 g., formic acid 0.68 g., succinic acid 8.35 g., lævulic acid 9.3 g., an unknown acid,  $C_8H_{14}O_6$ , m. p. 132—134°, 1.5 g., and another unknown acid,  $C_8H_{14}O_6$ , m. p. 191—192°, 0.5 g. From the products of the dry distillation of squalene under atmospheric pressure, isoprene and a colourless liquid, b. p. 62.5—65°/17 mm.,  $d_4^{20}$  0.8208,

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$n_D$  1.4621 (probably cyclodihydroxymyrcene), were isolated. By heating with a mixture of glacial acetic acid and 2% of concentrated sulphuric acid at 65–68° during three hours, squalene was found to be converted into an isomeride containing at least two rings. Further, squalene does not contain conjugated double bonds, and is easily reduced to a dodecahydro-derivative by hydrogen in the presence of platinum black. From these facts, the authors regard squalene as a higher aliphatic terpene, probably a dihydro-triterpene, and suggest the following formula for it as probable, but the nature of the right-hand group,  $\cdot\text{CH}(\text{C}_8\text{H}_{12})\cdot\text{CH}\cdot$ , is still not clear:



K. K.

**Action of Silver Sulphate in Sulphuric Acid Solution on Ethyl Bromide.** E. A. SCHULOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, 6, 233).—Alcohol is now found (cf. A., 1922, i, 913) among the products of the action of a sulphuric acid solution of silver sulphate on ethyl bromide, so that the ethylsulphuric acid formed evidently undergoes considerable hydrolysis. The conclusion is drawn that the reaction proceeds quantitatively in accordance with the equation  $\text{HAgSO}_4 + \text{EtBr} = \text{AgBr} + \text{EtHSO}_4$ .

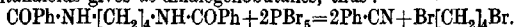
T. H. P.

**The Preparation of  $\alpha\delta$ -Dihalogen Derivatives of Butane.** C. S. MARVEL and A. L. TANENBAUM (*J. Amer. Chem. Soc.*, 1922, 44, 2645–2650; cf. von Braun, A., 1907, i, 127).—A good yield of  $\alpha\delta$ -dibromobutane may be obtained by the following series of reactions.  $\alpha\gamma$ -Dibromopropane is converted into  $\gamma$ -phenoxypropyl bromide by the action of sodium phenoxide, and this in turn into phenoxypropyl cyanide by the action of sodium cyanide. This cyanide is hydrolysed by alcoholic sulphuric acid, and the resulting ethyl phenoxybutyrate when reduced by sodium and absolute alcohol in toluene is converted into phenoxybutyl alcohol, b. p. 162–164°/19 mm.,  $n_D^{20}$  1.520, giving a *p*-nitrobenzoate, m. p. 91°. The alcohol, when heated with hydrobromic acid containing a little sulphuric acid, yields a mixture of  $\gamma$ -phenoxybutyl bromide, m. p. 41°, and the required  $\alpha\delta$ -dibromobutane, which may be separated by fractional distillation. In reducing ethyl phenoxybutyrate as described above (cf. Levene and Allen, A., 1917, i, 3), it is essential, if a high yield is to be obtained, to use alcohol that has been distilled first over calcium oxide and then over sodium, and to exclude all traces of moisture during the reduction. This method of reduction was also applied successfully to the reduction of esters of octoic, lauric, and myristic acids to the corresponding alcohols, and also to the reduction of certain cyanides to the corresponding primary amines.

W. G.

**Synthesis of Halogenated Compounds of the Butane Series.** JULIUS VON BRAUN and GEORG LEMKE (*Ber.*, 1922, 55, [B], 3526–3536).— $\alpha\delta$ -Dihalogenated butanes may be prepared conveniently

by oxidising *cyclohexanol* to adipic acid, conversion of the latter into the amide, and thence into the dibenzoyl derivative of  $\alpha\delta$ -aminobutane. Treatment of the latter compounds with phosphorus pentahaloids gives  $\alpha\delta$ -dihalogenobutanes, thus: . . .



The reaction in this case proceeds in exactly the same manner as with the dibenzoyl derivative of  $\alpha\epsilon$ -pentamethylenediamine and its higher homologues.

The oxidation of *cyclohexanol* to adipic acid (cf. Mannich and Hăncu, A., 1908, i, 245) is conveniently effected by the gradual addition of finely-divided potassium permanganate to a well-stirred suspension of *cyclohexanol* in aqueous sodium carbonate solution at 15–30°, the yield of acid being 70% of that theoretically possible. The acid is transformed by thionyl chloride at the atmospheric temperature into the corresponding chloride, which is converted by ammonia into the amide (yield 90%). The latter is converted by bromine and sodium hydroxide into  $\alpha\delta$ -diaminobutane, which, without being isolated, is further converted into the dibenzoyl derivative, m. p. 176–177°, the yield being 60%. Phosphorus pentabromide transforms the latter into  $\alpha\delta$ -dibromobutane, b. p. 80–82°/14 mm., in 70% yield. The similar action of phosphorus pentachloride gives a mixture of  $\alpha\delta$ -dichlorobutane and  $\delta$ -chlorobutylbenzamide,  $\text{Cl}[(\text{CH}_2)_4\cdot\text{NHBz}]$ , m. p. 54–55°.

$\alpha\delta$ -Dibromobutane reacts energetically with bromine in the presence of iron, yielding mainly  $\alpha\beta\gamma$ -tribromobutane, b. p. 102–103°/14 mm. The position of the bromine atoms is deduced from the observation that the compound reacts energetically with magnesium in the presence of ether, in accordance with the equations:  $2\text{C}_4\text{H}_9\text{Br}_2 + 3\text{Mg} = 3\text{MgBr}_2 + \text{C}_8\text{H}_{14}$  and  $\text{C}_4\text{H}_9\text{Br}_2 + 2\text{Mg} = \text{MgBr}_2 + \text{C}_4\text{H}_7\cdot\text{MgBr}$ . The former reaction predominates very greatly. If the product is treated with carbon dioxide, a hydrocarbon (or mixture of hydrocarbons),  $\text{C}_8\text{H}_{14}$ , and an acid,  $\text{C}_4\text{H}_7\cdot\text{CO}_2\text{H}$ , are obtained. The latter substance is present in too small quantity to permit its isolation, but its oxidation to methylmalonic acid shows it to have the constitution  $\text{CH}_3\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ . The hydrocarbon is oxidised to succinic acid, but does not appear to yield adipic acid. The course of the reaction differs entirely from that observed by von Braun and Deutsch (A., 1912, i, 106), and can only be explained simply on the assumption that the product is  $\alpha\beta\gamma$ -tribromobutane. Bromination of the  $\alpha\delta$ -compound, as in the case of  $\alpha\epsilon$ -dibromopentane (von Braun and Kirschbaum, A., 1920, i, 2), is accompanied by a displacement of a bromine atom. More vigorous bromination of  $\alpha\delta$ -dibromobutane leads to the production of  $\alpha\beta\gamma\delta$ -tetrabromobutane, m. p. 117°.

$\delta$ -Chlorobutylbenzamide, like the benzoyl derivative of  $\epsilon$ -chloro- $\alpha$ -methylamine, but unlike those of  $\gamma$ -chloropropylamine or  $\beta$ -chloroethylamine, reacts readily with aluminium chloride and benzene, yielding thereby *N*-benzoyl- $\delta$ -phenylbutylamine, m. p. 83° (cf. A., 1910, i, 819); the corresponding hydrochloride crystallises in leaflets, m. p. 159°.

*N*- $\delta$ -Chlorobutylbenzamide is transformed by diethylamine into

*N*-8-diethylaminobutylbenzamide,  $\text{NEt}_2(\text{CH}_2)_4\text{NHBz}$ , a colourless, viscous liquid, b. p.  $225\text{--}228^\circ/13\text{ mm.}$ , the salts of which exhibit little tendency to crystallise. It is hydrolysed by concentrated hydrochloric acid to 8-diethylaminobutylamine, a colourless, fairly mobile liquid, b. p.  $78\text{--}79^\circ/13\text{ mm.}$  (picrate, yellow needles, m. p.  $157^\circ$ ; chloroplatinate, yellow crystals, m. p.  $195^\circ$ ); it is remarkable that the base does not react with nitrous acid.

Sodium benzoisulphinide is converted by ethylene dibromide at  $170\text{--}180^\circ$  almost entirely into *N*-β-bromoethylbenzoisulphinide,  $\text{C}_6\text{H}_5\text{--}\langle\text{SO}_2\text{--CO}\rangle\text{N--CH}_2\text{--CH}_2\text{Br}$ . Under precisely similar conditions, trimethylene bromide gives α-*dibenzoisulphinidopropane*, a crystalline powder, m. p.  $196^\circ$ , in 47% yield. Tetramethylene bromide behaves similarly to the trimethylene compound, giving αδ-*dibenzoisulphinidobutane*,  $\text{C}_6\text{H}_5\text{--}\langle\text{SO}_2\text{--CO}\rangle\text{N--(CH}_2\text{)}_4\text{N--}\langle\text{SO}_2\text{--CO}\rangle\text{C}_6\text{H}_5$ , m. p.  $204\text{--}206^\circ$ , in 40% yield. H. W.

**Unsaturated Residues in Chemical and Pharmacological Relationship.** III. JULIUS VON BRAUN and GEORG LEMKE (*Ber.*, 1922, 55, [B], 3536--3559; cf. von Braun and Köhler, A., 1918, i, 162; von Braun and Braunsdorf, A., 1921, i, 772).—A further examination of the possibility of an intimate connexion between the peculiar physiological activity of compounds containing the allyl group, the relatively weak union of allyl with oxygen, nitrogen, sulphur, and halogen, and the β-γ-position of the double bond. The latter appears to be important in its effect on the physiological activity of the substances, since *N*-cinnamyl norcodeine is exactly analogous to *N*-allylnorcodeine in its antagonistic action towards morphine.

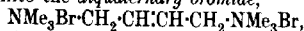
An extended study has been made of compounds containing the group  $\text{--CH}_2\text{--CH=CH--CH}_2\text{--}$ , since this may be regarded in a measure as a doubled allyl, and also because cases of *cis*- and *trans*-isomerism are to be expected. In the latter respect, the experiments are disappointing, since the initial material, *cis*-butadiene dibromide, is found to be unusually labile and to pass under the influence of a great variety of chemical reagents into the *trans*-modification of which it gives derivatives. The comparison of a series of compounds,  $\text{CH}_2\text{X--CH=CH--CH}_2\text{X}$ , with a similar series of substances,  $\text{CH}_2\text{X--CH}_2\text{--CH}_2\text{--CH}_2\text{X}$ , shows in general that the butadiene closely resemble the allyl derivatives in respect of the feeble union of the unsaturated carbon chain with halogen, oxygen, nitrogen, and sulphur. As is to be expected, the unsaturated compounds show less tendency to form the thiophene ring than does the saturated butane derivative, but, on the other hand, its ability to yield a pyrroline derivative (although only in small yield) is somewhat surprising.

When compared with the simpler allyl compounds, the butenyl compounds are unusually inactive physiologically, so that the chemical analogy of the substances is not accompanied by pharmacological analogy. This result appears to be due either to the

great increase in the size of the molecule or to the spatial proximity of the physiologically active centres in the presence of the chain  $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot$ , which is such as to cause mutual disturbance.

*N*-Cinnamylnorcodeine,  $\text{OMe}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OH})\text{N}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHPh}$ , a colourless substance, m. p.  $78^\circ$  after softening at  $74^\circ$ , is prepared by the treatment of a solution of norcodeine in chloroform with cinnamyl bromide at  $100^\circ$ ; the sulphate, hydrochloride, and chloroplatinate, a pale yellow powder, decomp.  $208^\circ$ , are described.

For the preparation of  $\alpha\delta$ -dibromo- $\Delta^2$ -butene,  $\alpha\beta\gamma\delta$ -tetrabromobutane is debrominated with zinc dust and alcohol, the  $\Delta^{\gamma\delta}$ -butadiene which is evolved is dissolved in chloroform and treated with one molecular proportion of bromine. The mixture of stereoisomerides thus produced is separated by rapid distillation under diminished pressure into the previously described solid *trans*- $\alpha\delta$ -dibromo- $\Delta^2$ -butene, b. p. about  $78\text{--}80^\circ/13$  mm., m. p.  $53^\circ$ , and *cis*- $\alpha\delta$ -dibromo- $\Delta^2$ -butene, b. p.  $59^\circ/13$  mm., which does not solidify in a freezing mixture of ice and salt. The constitution of the latter substance is now elucidated by the observation that it is oxidised by permanganate to a liquid glycol and finally to bromoacetic acid, but it appears doubtful whether the compound as thus prepared is quite homogeneous. It passes into the solid *trans*-modification slowly at the atmospheric temperature, rapidly when heated. The change is catalytically accelerated in particular by halogen acids, and to a smaller extent by sulphuric acid. The addition of hydrogen bromide to  $\alpha\delta$ -dibromo- $\Delta^2$ -butene is effected by protracted heating of the substance with a fuming solution of hydrogen bromide in glacial acetic acid at  $100^\circ$  (it is immaterial which modification of the dibromo-compound is used), whereby  $\alpha\beta\delta$ -tribromobutane, b. p.  $108\text{--}112^\circ/14$  mm., is produced in 65% yield (cf. von Braun and Deutsch, A., 1912, i, 106).  $\alpha\delta$ -Dibromo- $\Delta^2$ -butene is hydrolysed much more rapidly than  $\alpha\delta$ -dibromobutane by hot water. It is rapidly transformed by trimethylamine in the presence of benzene at  $20^\circ$  into the *diquaternary bromide*,

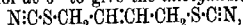


a very hygroscopic solid, m. p. about  $295\text{--}300^\circ$  (the corresponding chloroplatinate is a yellow powder, m. p.  $246^\circ$ ); under similar conditions of time, temperature, and concentration,  $\alpha\delta$ -dibromobutane remains unaffected, but when more drastically treated it becomes converted into the substance  $\text{NMe}_3\text{Br}\cdot[\text{CH}_2]_4\cdot\text{NMe}_3\text{Br}$ , m. p.  $295^\circ$ .  $\alpha\delta$ -Dibromobutane does not react with an ethereal solution of magnesium phenyl bromide, even on protracted heating; under similar conditions,  $\alpha\delta$ -dibromo- $\Delta^2$ -butene is fairly readily transformed into  $\gamma$ -benzylallyl bromide,  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ , b. p.  $112\text{--}115^\circ/14$  mm. Treatment of  $\alpha\delta$ -dibromo- $\Delta^2$ -butene with a large proportion of the Grignard's reagent leads to the production of  $\alpha\delta$ -diphenyl- $\Delta^2$ -butene, which, however, could not be separated completely from diphenyl.

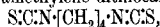
$\alpha\delta$ -Diphenoxy- $\Delta^2$ -butene,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OPh}$ , m. p.  $83\text{--}84^\circ$ , is readily prepared by boiling  $\alpha\delta$ -dibromo- $\Delta^2$ -butene with an alcoholic solution of sodium phenoxide. In striking contrast to  $\alpha\delta$ -diphenoxybutane, the unsaturated compound is extensively

decomposed at its boiling point, but it was not found possible to isolate the presumable product  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  of the change or any of its derivatives in the homogeneous condition.

$\alpha\delta$ -Dibromo- $\Delta^2$ -butene reacts readily with ammonium thiocyanate dissolved in alcohol at  $0^\circ$  to give the *thiocyanate*,



prisms, m. p.  $82^\circ$ ; the constitution of the compound follows from the observations that it is indifferent towards bases, gives an intense odour of mercaptan when treated with zinc and hydrochloric acid, and is converted by thiobenzoic acid into the *dithiourethane*,  $\text{NH}_2\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NH}_2$ , m. p.  $165^\circ$  (decomp.). The thiocyanate is relatively very stable towards rise in temperature, differing in this respect from allyl thiocyanate; at  $150^\circ$ , however, it rapidly undergoes a complex change which does not lead to well-defined products. *Tetramethylene dithiocyanate*, b. p.  $193\text{--}195^\circ/14\text{ mm.}$ , is readily prepared in the usual manner; it is converted by thiobenzoic acid into tetramethylene bisdithiourethane, m. p.  $154^\circ$  (cf. von Braun, A., 1910, i, 13). For the preparation of tetramethylene dithiocarbimide,



a solution of tetramethylenediamine in alcohol is treated with carbon disulphide (whereby *tetramethylene dithiocarbamate*, m. p.  $150^\circ$ , is slowly precipitated) and subsequently with iodine, a solution of sodium in alcohol, and again with iodine; the *dithiocarbimide* is thus obtained as a yellow liquid which could not be caused to solidify. It is very unstable, and decomposes slowly when preserved at the atmospheric temperature, rapidly and completely when warmed. With aniline, it yields *NN'-diphenyltetramethylenedithiocarbimide*,  $\text{C}_6\text{H}_5(\text{NH}\cdot\text{CS}\cdot\text{NHPh})_2$ , m. p.  $169^\circ$ ; with an alcoholic solution of methylamine it gives *NN'-dimethyltetramethylenedithiocarbimide*, a crystalline powder, m. p.  $128^\circ$ , whilst with ammonia dissolved in alcohol it yields *tetramethylenedithiocarbimide*,  $\text{C}_4\text{H}_8(\text{NH}\cdot\text{CS}\cdot\text{NH}_2)_2$ , m. p.  $198^\circ$ .

The action of cyanogen bromide on an ethereal solution of  $\alpha\delta$ -tetramethyldiamino- $\Delta^2$ -butene leads to the production of *trans*- $\alpha\delta$ -dibromo- $\Delta^2$ -butene, dimethylcyanamide, and the quaternary compound,  $\text{NMe}_2\text{Br}\cdot\left\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3 \end{array}\right\rangle\text{NMe}_2\text{Br}$ , m. p.  $242^\circ$  (*chloroplatinate*, golden-yellow octahedra, m. p.  $294^\circ$ ). Since the possibility existed that the latter substance might in reality be *N*-dimethylpyrrolinium bromide,  $\left\langle\begin{array}{c} \text{CH}\cdot\text{CH}_2 \\ \text{CH}\cdot\text{CH}_2 \end{array}\right\rangle\text{NMe}_2\text{Br}$ , the latter was

prepared by the action of two molecular proportions of dimethylamine on a solution of  $\alpha\delta$ -dibromo- $\Delta^2$ -butene in benzene at  $100^\circ$ ; in contrast to the substance just described, it is a liquid which does not solidify even when strongly cooled (*chloroplatinate*, m. p.  $242^\circ$ ).  $\alpha\delta$ -Tetramethyldiaminobutane cannot be prepared directly from the corresponding bromide and dimethylamine, since the tendency towards ring formation is so great that *N*-dimethylpyrrolinium bromide is produced even when a large excess of the base is used. The ditertiary base, b. p.  $169^\circ$ , is, however, pre-

pared in very moderate yield by the decomposition of *NN'*-hexamethyltetramethylenediammonium hydroxide (cf. Willstätter and Heubner, A., 1907, i, 959); an unsaturated base, probably  $\delta$ -dimethylamino- $\Delta^8$ -butene,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , b. p.  $82-85^\circ$ , is formed as by-product. The ditertiary base reacts energetically with cyanogen bromide, with elimination of methyl bromide from one or both ends of the molecule.

$\alpha\delta$ -Dibromobutane is converted quantitatively by aniline into 1-phenylpyrrolidine,  $\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} > \text{NPh}$ , b. p.  $124^\circ/14$  mm., a colourless liquid which rapidly becomes brown when exposed to air; it gives a *picrate*, m. p.  $114^\circ$ , and a *methiodide*, m. p.  $150^\circ$ . Under precisely similar conditions,  $\alpha\delta$ -dibromo- $\Delta^8$ -butene gives minimal quantities of 1-phenyl- $\Delta^8$ -pyrroline,  $\begin{smallmatrix} \text{CH}\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}\cdot\text{CH}_2 \end{smallmatrix} > \text{NPh}$ , a mixture of compounds formed by the action of several dibromide and aniline molecules and  $\alpha\delta$ -dianilino- $\Delta^8$ -butene,

$\text{NPh}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{NPh}$ ,  
a viscous liquid, b. p. above  $300^\circ/14$  mm., which is conveniently characterised as the *bis-nitrobenzoyl* derivative, slender needles, m. p.  $210^\circ$ .

When boiled with an aqueous alcoholic solution of potassium sulphide (under the conditions which lead to the production of tetrahydrothiophen from  $\alpha\delta$ -dibromobutane),  $\alpha\delta$ -dibromo- $\Delta^8$ -butene is converted into a complex, caoutchouc-like mass.

4-Pyrrolidinopantipyrene, m. p.  $128^\circ$ , is prepared by warming  $\alpha\delta$ -dibromobutane with 4-aminoantipyrene on the water-bath or from its components in alcoholic solution; the corresponding *hydrochloride* and *methiodide* could not be caused to crystallise. 4-Aminoantipyrene and  $\alpha\delta$ -dibromo- $\Delta^8$ -butene in the presence of acetone give complex products of high molecular weight and (in 40% yield), 4- $\Delta^8$ -pyrrolinoantipyrene, m. p.  $155^\circ$ .

$\gamma$ -Hydroxypropyldimethylamine reacts fairly readily with  $\alpha\delta$ -dibromobutane at  $100^\circ$  to yield *NN'*-tetramethyl-*NN'*-di- $\gamma$ -hydroxypropyltetramethylenediammonium bromide,

$\text{C}_4\text{H}_8(\text{NMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ ,  
m. p.  $194^\circ$ , and with  $\alpha\delta$ -dibromo- $\Delta^8$ -butene in benzene solution to give *NN'*-tetramethyl-*NN'*-di- $\gamma$ -hydroxypropyl- $\Delta^8$ -butenylenediammonium bromide, a very hygroscopic solid, m. p.  $188^\circ$  (*chloroplatinate*, m. p.  $213^\circ$ ).

$\alpha\delta$ -Dibromo- $\Delta^8$ -butene is converted by an excess of norcodeine dissolved in chloroform into  $\alpha\delta$ -dinorcodeyl- $\Delta^8$ -butene,

$\text{C}_4\text{H}_6[\text{N}:\text{C}_{16}\text{H}_{14}\text{O}(\text{OH})\cdot\text{OMe}]_2$ ,  
m. p.  $132^\circ$  after softening at  $125^\circ$ ; the corresponding *sulphate*, *hydrochloride*, *chloroplatinate*, and *picrate* are described.  $\alpha\delta$ -Dibromobutane and norcodeine, on the other hand, give exclusively *norcodeiniumpyrrolidinium bromide*,  $\text{C}_4\text{NH}_8\text{Br}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OH})\cdot\text{OMe}$ .

$\alpha\delta$ -Dibromobutane, hydrocyprine, and alcoholic potassium hydroxide solution give  $\alpha\delta$ -dihydrocyprylbutane,  $\gamma$  decomp.  $232^\circ$ , in 56% yield. In similar circumstances,  $\alpha\delta$ -dibromo- $\Delta^8$ -butene

yields  $\alpha\delta$ -dihydrocupreyl- $\Delta^8$ -butene, m. p. 215—218° after becoming black at 200°. H. W.

**A Synthesis of  $\beta$ -Chloroallyl Chloride.** ARTHUR J. HILL and EDWIN J. FISCHER (*J. Amer. Chem. Soc.*, 1922, 44, 2582—2595).—Starting from glycerol,  $\beta$ -chloroallyl chloride may be prepared with good yields by the following procedure. The glycerol, previously dehydrated, is saturated with dry hydrogen chloride after the addition of glacial acetic acid to the extent of 6% of its weight as a catalyst. The  $\alpha\gamma$ -dichlorohydrin mixed with a small amount of the  $\alpha\beta$ -isomeride is converted into epichlorohydrin by pouring it into 30% aqueous sodium hydroxide at 12—15°. The epichlorohydrin is then reconverted into the  $\alpha\gamma$ -dichlorohydrin by the action of concentrated hydrochloric acid. To 300 g. of the dichlorohydrin are added 240 g. of phosphoryl chloride and the mixture is heated on a water-bath for three hours and then for five hours at 180°, after which it is distilled under slightly diminished pressure. Between 225° and 230°,  $\beta$ -chloroallyl chloride distils over. Phosphoric oxide may be used instead of the oxychloride, but the yield is thereby considerably reduced. In either case, the dehydration of the dichlorohydrin is preceded by ester formation, and the higher temperature is necessary for the decomposition of these intermediate products. Other dehydrating agents tried were potassium hydrogen sulphate, sulphuric acid, oxalic acid, boric anhydride, thionyl chloride, and phosphorus trichloride, but in no case could the chloroallyl chloride be obtained.

$\beta$ -Chloroallyl chloride may be used for the alkylation of malonic esters, and the following compounds have been prepared. *Diethyl chloroallylmalonate*, b. p. 161—163°/12 mm., *diethyl di(chloroallyl)malonate*, b. p. 190°/12 mm. or 300°/760 (decomp.), and *diethyl ethylchloroallylmalonate*, b. p. 157—160°/12 mm. W. G.

**Purification of Methyl Alcohol by means of Sodium Hypochlorite.** ROBERT CHARLES MENZIES (*T.*, 1922, 121, 2787—2793).

**Union of Hydrogen with Acetylene Derivatives. XIII. Mechanism of the Catalytic Hydrogenation of Dimethylhexinenediol.** J. S. ZALKIND and (Mlle) M. S. PESCHEROKOVA (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 186—190).—The values obtained by Zalkind and Pischtschikov (*A.*, 1915, ii, 435) for the velocity of hydrogenation of tetramethylbutinenediol in presence of colloidal palladium showed that, as the reaction proceeds, the value of  $k$ , calculated from the formula for unimolecular reactions, at first increases. Such increase was regarded as due to the gradual removal of the acetylenic glycol. Further experiments show that this is not the case. The velocity of the reaction is found to be greatly increased if the palladium is first saturated with hydrogen and then left for some time (sixty hours) in contact with the acetylenic glycol prior to commencement of the hydrogenation. The retardation of the hydrogenation in its early stages is evidently due to the formation, either chemically or by adsorption, of intermediate compounds. "H. P.

**Equilibrium in Systems Composed of Water and Alcohols : Methyl Alcohol, Pinacone, Glycerol, and Erythritol.** NICOLAI ANTONOVICH PUSHIN and ALEXANDRA ALEXANDROVNA GLAGOLEVA (T., 1922, 121, 2813—2822).

**Catalytic Dehydration of Alcohols in the Wet Way. I. Olefines and Cyclenes.** J. B. SENDERENS (*Ann. Chim.*, 1922, [ix], 18, 117—145; cf. A., 1912, i, 406).—A review of the author's work on this subject (A., 1910, i, 649, 651; 1912, i, 331, 441), from which the conclusion is drawn that, of the available catalysts, aluminium sulphate and potassium hydrogen sulphate are of restricted application whilst concentrated sulphuric acid is effective in almost all cases. Theoretically, the dry method of catalysis is more efficient, but in practice the wet method is preferable, owing to its rapidity and the ease with which it may be carried out. H. J. E.

**Catalytic Dehydration of Alcohols in the Wet Way. II. Ester-formation.** J. B. SENDERENS and J. ABOULENO (*Ann. Chim.*, 1922, [ix], 18, 145—188; cf. preceding abstract, *Ann. Berthelot*, A., 1879, 866, and Fischer and Speier, A., 1896, i, 201).—A general review of the authors' work (A., 1911, i, 600, 637; 1912, i, 694; 1913, i, 41, 42; 1914, i, 379) shows that concentrated sulphuric acid is by far the most advantageous catalyst, operating efficiently in all the different variations of the general reaction. H. J. E.

**Vapour Pressures, Densities, and some Derived Quantities for Ethyl Ether at Low Temperatures.** ROBERT S. TAYLOR and LEIGHTON B. SMITH (*J. Amer. Chem. Soc.*, 1922, 44, 2450—2463).—The densities and vapour pressures of ethyl ether have been measured over the lower range of temperature. The following density values are recorded:  $-120^{\circ}$ , 0.86195;  $-110^{\circ}$ , 0.85192;  $-80^{\circ}$ , 0.82141;  $-75^{\circ}$ , 0.81640;  $-70^{\circ}$ , 0.81114;  $-50^{\circ}$ , 0.79032;  $-45^{\circ}$ , 0.78510;  $-40^{\circ}$ , 0.77970;  $-35^{\circ}$ , 0.77425;  $0^{\circ}$ , 0.73629;  $20^{\circ}$ , 0.71349;  $35^{\circ}$ , 0.69576;  $40^{\circ}$ , 0.68979;  $55^{\circ}$ , 0.67116, and  $60^{\circ}$ , 0.66501. It is found that the density above  $0^{\circ}$  is represented by the equation  $d=73629-0.001138t-0.000001237t^2$ , and that below  $0^{\circ}$  by  $d=0.73629+0.0011044t-0.0000004772t^2$ . From these equations, the density and specific volume have been calculated for every  $5^{\circ}$  from  $-120^{\circ}$  to  $+70^{\circ}$  and the values compared with the present results and those of other investigators. The recorded vapour pressure values are:  $-60.799^{\circ}$ , 3.95 mm.;  $-55.748^{\circ}$ , 5.93 mm.;  $-50.873^{\circ}$ , 8.77 mm.;  $-45.998^{\circ}$ , 12.62 mm.;  $-41.125^{\circ}$ , 17.78 mm.;  $-36.231^{\circ}$ , 24.77 mm.;  $-31.329^{\circ}$ , 34.03 mm.;  $-26.421^{\circ}$ , 45.81 mm.;  $-21.502^{\circ}$ , 61.31 mm.;  $-16.578^{\circ}$ , 80.67 mm.;  $-11.637^{\circ}$ , 104.79 mm.;  $-6.698^{\circ}$ , 134.76 mm.;  $+0.009^{\circ}$ , 186.13 mm.;  $+4.975^{\circ}$ , 233.73 mm.;  $+9.937^{\circ}$ , 290.62 mm.;  $+14.903^{\circ}$ , 358.15 mm.;  $+19.871^{\circ}$ , 437.70 mm. It is found that the vapour pressures between  $-60^{\circ}$  and  $+20^{\circ}$  are given by the equation  $\log p = -(2168.599/T) + 13.882702 - 0.01814165T + 0.000017181957T^2$ , and by means of this formula the values of the vapour pressure have been calculated for every five degrees over the range  $-65^{\circ}$

to  $+25^{\circ}$  and the values compared with the present experimental values. From the above-mentioned data and an equation of condition, the latent heats of evaporation and the change in internal energy on evaporation have been calculated. A relationship connecting the specific volume of the liquid and the internal energy change on evaporation is given. From the latent heats there was obtained the difference in saturation specific heats of the vapour and liquid, and from these, when compared with Regnault's values for the liquid, some values of the specific heat of the vapour at constant pressure were deduced. J. F. S.

**The Oxidation of  $\alpha\delta$ - and  $\alpha\epsilon$ -Oxides.** ADOLF FRANKE and FRITZ LIEBEN (*Monatsh.*, 1922, 43, 225—236).—The oxidation with potassium permanganate of a number of anhydrides of  $\alpha\delta$ - and  $\alpha\epsilon$ -glycols was studied to determine whether it would be possible to deduce the constitution of such compounds from their oxidation products.  $\alpha\epsilon$ -Oxidopentane was converted smoothly into glutaric acid whilst  $\alpha\epsilon$ -oxidoheptane gave principally succinic and acetic acids, rupture of the ring taking place between the  $\delta$  and  $\epsilon$  carbon atoms. The latter oxidation therefore follows the same lines as that of  $\alpha\delta$ -oxidopentane, which gave principally acetic and oxalic acids (not the expected malonic acid), and only to a small extent formic and succinic acids. It is noteworthy that the  $\alpha\epsilon$ -oxidoheptane prepared from 1:5-hexandiol was identical with that previously prepared from 1:6-hexandiol (*Monatsh.*, 1914, 35, 931). This follows, not only from their similar physical properties, but also from their identical oxidation products. When the oxide contains a tertiary carbon atom, oxidation goes only as far as the lactone; thus  $\beta\gamma$ -oxido- $\beta$ -methylhexane gives  $\delta$ -methylhexolactone,  $\text{OMe}(\text{CH}_2)_3\text{CO}$ , and only very little acetone and succinic acid.

E. H. R.

**Trichloroethyl Carbamate.** R. WILLSTÄTTER, W. DUISBERG, and T. CALLSEN (U.S. Pat. 1427506).—*Trichloroethyl carbamate*, white needles, m. p.  $64$ — $65^{\circ}$ , is obtained by interaction of carbamyl chloride and trichloroethyl alcohol in ethyl ether solution.

CHEMICAL ABSTRACTS.

**Researches on Residual Affinity and Co-ordination. XIV. Interactions of Metallic Salts and Dimethyldithiolethylene.** GILBERT T. MORGAN and WILFRID LEDBURY (*T.*, 1922, 121, 2882—2894).

**Synthesis of Alkylidenecyanoacetic Acids and of Substituted Succinic Acids. II. Preparation of Acids containing Saturated Aliphatic Residues and the Constitution of the Aliphatic Alkylidenecyanoacetic Esters.** ARTHUR LAPWORTH and JOHN ALEXANDER McRAE (*T.*, 1922, 121, 2741—2755).

**Catalytic Hydrogenation and the Potential of the Hydrogen Electrode.** JAMES B. CONANT and HAROLD B. CUTTER (*J. Amer. Chem. Soc.*, 1922, 44, 2651—2654).— $\beta\beta$ -Dimethylacrylic acid

can be hydrogenated in 0.1N-hydrochloric acid solution by hydrogen in the presence of a catalyst, but is not reduced by chromous chloride in aqueous solution, although the reducing power of the latter reagent, as measured by its oxidation-reduction potential, is 0.3 volt greater than that of the former reagent. Maleic acid is reduced by chromous chloride, but not by sodium hyposulphite, whilst dibenzoyl ethylene is reduced by both reagents. As a result of these tests, the authors consider that the process of catalytic hydrogenation cannot be successfully formulated in terms of oxidation-reduction potentials. It is suggested that in one case there is a process of hydrogenation, that is, the simple adding on of hydrogen atoms, whilst in the other case there is reduction, that is, the process involves electron addition and is of an irreversible type.

W. G.

**Unsaturated Fatty Acids of Brain Cephalins.** P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1922, **54**, 91—98).—An investigation of the fatty acids of brain cephalin on the lines recently applied to lecithin (cf. A., 1922, i, 621) has shown that stearic, oleic, and arachidonic acids are present in cephalin. Other saturated and unsaturated acids are also present, but have not yet been isolated in a pure state. No evidence has been obtained of the presence of linolic acid.

E. S.

**Unsaturated Fatty Acids of Brain Lecithins.** P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1922, **54**, 99—100).—The fatty acids from brain lecithin contain oleic and arachidonic acids.

E. S.

**Preparation and Properties of Tri-iodopyruvic Acid.** M. GARINO and E. ZUNINI (*Gazzetta*, 1922, **52**, ii, 220—225).—Tri-iodopyruvic acid,  $C_3H_3O_4I_3$ , prepared by treating pyruvic acid with iodic and hydriodic acids, forms lemon-yellow crystals with a slightly pungent odour, m. p. about 97°. It is highly unstable, especially in contact with organic substances and under the influence of light; its aqueous solution is relatively stable if iodic acid is present.

T. H. P.

**Glucinum Compounds.** JULIUS MEYER and ERWIN MANTEL (*Z. anorg. Chem.*, 1922, **123**, 43—55).—Glucinum salts of organic acids are very difficult to obtain in the pure crystalline form; the composition, properties, and constitution of many of these salts have not been clearly proved. The authors attempted to prepare the malonate, but were unable to obtain the pure product. They were, however, able to prepare some double salts, to which they assign the constitution  $[Gl(CH_2(CO_2)_2)_2]K_2$ ,  $[Gl(CH_2(CO_2)_2)_2]Na_2 \cdot H_2O$ , and  $[Gl(CH_2(CO_2)_2)_2](NH_4)_2$  (cf. Wirth, A., 1914, i, 657). The authors discuss the constitution of basic glucinum acetate and they argue that Glasmann's structure (cf. A., 1908, i, 120) cannot be accepted. Biltz's suggestion,  $[Gl(\overset{HO}{\underset{HO}{|}}|)_3]OAc$ , is also shown to be untenable. The present authors suggest  $[GlO(Gl(OAc)_2)_3]$ . They were, however, unable to find much support for this structure.

W. T.

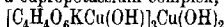
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**Tervalent Manganese. III.** JULIUS MEYER and WALTER SCHRAMM (*Z. anorg. Chem.*, 1922, 123, 56—68).—Diaquo-dimalonatomanganic acid was prepared,  $[\text{Mn}(\text{H}_2\text{O})_2(\text{CH}_2(\text{CO}_2)_2)_2]\text{H}$ , as well as its lithium, sodium, potassium, rubidium, and ammonium salts. These compounds are olive-green, they dissolve in water, forming yellow solutions, and they are readily hydrolysed with the separation of manganic hydroxide. The potassium salt of trimalonatomanganic acid,  $[\text{Mn}(\text{CH}_2(\text{CO}_2)_2)_3]\text{K}_3$ , was prepared from the above potassium salt. This substance is red, but from a concentrated solution, especially in the presence of malonic acid, green crystals of the potassium diaquo-dimalonatomanganate separate. The tri-lithium, -sodium, and -ammonium salts could not be obtained in a pure state owing to their very high solubility. The tripotassium salt was found to be stable towards light (cf. the analogous oxalate). The colour and constitution of manganic salts are briefly discussed. W. T.

**Formation of  $\gamma$ -Alkylidene Derivatives from Ethylidene-malonic Ester.** LUCY HIGGINBOTHAM and ARTHUR LAPWORTH (*T.*, 1922, 121, 2823—2830).

**The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. V. Products Derived from  $\alpha$ -Halogenated  $\beta$ -Methylglutaric Acids.** CHRISTOPHER KELK INGOLD (*T.*, 1922, 121, 2676—2695).

**The Neutralisation of Tartaric Acid in Presence of Metallic Chlorides. Neutral and Buffer Zones.** L. J. SIMON (*Compt. rend.*, 1922, 175, 887—890; cf. Simon and Zivy, *A.*, 1922, ii, 880).—A mixture of potassium tartrate and potassium hydrogen tartrate constitutes a buffer solution, and the author has studied the effect of adding to it copper, zinc, and ferric chlorides. In the case of copper, the buffer effect increases and the results obtained point to the existence of a cupropotassium complex,

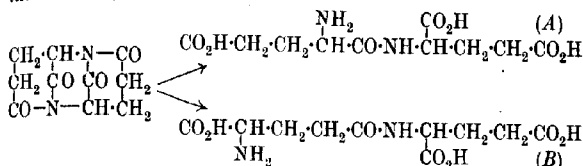


(cf. Masson and Steele, *T.*, 1899, 75, 725). Although a complex,  $\text{C}_4\text{H}_4\text{O}_6\text{KZn}\cdot\text{OH}$ , may be formed on addition of zinc chloride, the buffer effect is unaltered, but the presence of ferric chloride leads to a marked decrease of the zone in which the effect is obtained.

H. J. E.

**The Action of Glycerol on Glutamic Acid when Heated. Formation of *cyclo*Glutamylglutamic Acid (2:5-Diketopiperazine-3:6-dipropionic Acid) and of Glutamylglutamic Acid.** A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1922, [iv], 31, 1045—1063).—The condensation of glutamic acid in presence of glycerol (cf. Abderhalden and Kautzsch, *A.*, 1910, i, 230, 768) was effected on heating at 170° for eight hours, yielding a product which was separated as barium salt by addition of baryta water. The product is not a polyglutamic acid analogous to the polyaspartic acids (cf. Schaal, *A.*, 1871, 129; also Schiff, *A.*, 1898, i, 67; 1899, i, 195), but 2:5-diketopiperazine-3:6-dipropionic acid. By treat-

ment with aqueous sodium hydroxide, the substance was converted into glutamic acid, passing through the intermediate stage of glutamylglutamic acid. The latter was separated by Fischer's original method, and on evaporation from alcohol-water mixture yielded an amorphous mass, m. p. 167—168°. From a consideration of the constitution of the *cyclo*-acid, it is probable that cleavage of the molecule may occur in two ways (cf. Ravenna, A., 1922, i, 180) and that the acid thus obtained is a mixture of the two possible products. The reaction is shown structurally as follows, the formula A representing the substance which forms the bulk of the mixture :



H. J. E.

**The Preparation of Ethanetetracarboxylic Acid.** C. MANNICH and ERICH GANZ (*Ber.*, 1922, 55, [B], 3509—3510).—The preparation of ethanetetracarboxylic acid in moderate amount by the hydrolysis of the corresponding ester is greatly hampered by the difficulty of effecting the reaction by acid or alkali in a satisfactory manner (cf. Philippi and Hanusch, A., 1920, i, 594). It is therefore preferable to obtain the acid by the catalytic hydrogenation of ethylenetetracarboxylic acid dissolved in acetone in the presence of palladised charcoal. The elimination of carbon dioxide during the process cannot be completely avoided, but the pure acid, m. p. 167—169° (decomp.), can be isolated by repeated crystallisation of the crude product from acetone. H. W.

**The Action of Hydrogen Peroxide on Formaldehyde.**  
**The Theory of Oxidative Processes.** A. BACH and A. GENEROSOW (*Ber.*, 1922, 55, [B], 3560—3566).—Formaldehyde is oxidised by hydrogen peroxide to formic acid and hydrogen. The latter must be derived either from the water or the hydrogen peroxide, and since it is also obtained by the use of other hydrogen-free oxidising agents (potassium chromate, potassium permanganate, lead oxide) in alkaline solution, it appears valid to assume that it originates from the water. The hydrogen peroxide appears to be protected from reduction by the liberated hydrogen by the formation of a complex compound with formaldehyde, the reduction of which is a slower process than the union of the hydrogen atoms to molecules. The interpretation of the course of the reaction in accordance with Traube's theory of oxidation in the presence of water assumes that the formaldehyde molecule in consequence of the removal of a hydrogen atom by oxidation acquires the power of combining with a hydroxyl-ion with the production of formic acid and liberation of the equivalent quantity of hydrogen, whereas

Wieland's theory requires that the formaldehyde hydrate molecule should be able by partial dehydrogenation to decompose spontaneously into formic acid and hydrogen, thus:  $\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2(\text{OH})_2$ .  $2\text{CH}_2(\text{OH})_2 + \text{H}_2\text{O}_2 = 2\text{CH}(\text{OH})_2 + 2\text{H}_2\text{O}$ .  $2\text{CH}(\text{OH})_2 = 2\text{CH}_2\text{O} + \text{H}_2$ . The observed facts are best interpreted by the former theory.

Wieland's application of the dihydrogenation theory to biological oxidative processes is criticised at length. The experimental foundation of Wieland's assumption of the identity of oxidising and reducing ferments rests on observations with tissues and their extracts, which are unsuitable for the purpose, since they show not only oxidising and reducing but also hydrolytic properties. In spite of many attempts, it has not been found possible to effect a reduction with purified peroxydase.

H. W.

**Preparation of  $\alpha$ -Trioxymethylene and a New Polymeride of Formaldehyde.** DALZIEL LLEWELLYN HAMMICK and ALFORD REGINALD BOEREE (T., 1922, 121, 2738—2740).

**Preparation of Acetaldehyde.** E. WERTHEIM (*J. Amer. Chem. Soc.*, 1922, 44, 2658—2659).—Certain modifications are suggested in the method of Adams and Williams (cf. A., 1922, i, 222) for the preparation of acetaldehyde by the oxidation of alcohol. The mechanical stirring is replaced by a steady stream of carbon dioxide. The oxidising agent recommended is a mixture of 115 g. of nitric acid (*d* 1.42), 60 g. of sodium dichromate, 20 g. of sulphuric acid (*d* 1.84), and 220 c.c. of water, these quantities sufficing to oxidise 25 g. of alcohol. The alcohol is heated to boiling and the oxidising mixture is run slowly into it, the time taken being about twenty minutes.

W. G.

**A New Extractive and Absorptive Medium for Scientific and Technical Purposes.** GERHARD SCHMITT (*Petroleum Times*, 1922, 8, 249—250).—A solution of sulphur dioxide in acetone (equal parts) has great solvent power for unsaturated organic compounds and resinous substances, and possesses all the advantages of liquid sulphur dioxide whilst it is more convenient to manipulate. It is easily recovered by distillation, there being practically no chemical action on the extracted substance; moreover, extraction can be carried out at low temperatures in an open vessel. Its application to the extraction of soluble substances from coal, lignite, etc., is specially mentioned.

CHEMICAL ABSTRACTS.

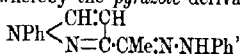
**Ethoxymethylenediacyl** [ $\alpha$ -Ethoxy- $\Delta^5$ -pentene- $\gamma$ -dione] and  $\alpha$ -Ethoxyethylane- $\gamma$ -dione. OTTO DIELS and JUSTUS PETERSEN (*Ber.*, 1922, 55, [B], 3449—3457).—The only representative of the simple  $\alpha\beta$ -unsaturated 1:2-diketones which has been described previously is styryl methyl diketone,  $\text{CHPh}:\text{CH}\cdot\text{CO}\cdot\text{CO}\cdot\text{Me}$  (Diels and Andersonn, A., 1911, i, 464; Diels and Sharkoff, A., 1913, i, 875). A second member of this class, ethoxymethylenediacyl, has now been prepared and examined.

*Ethoxymethylenediacetyl* [ $\alpha$ -ethoxy- $\Delta^5$ -pentene- $\gamma\delta$ -dione],

is prepared in poor yield by the action of ethyl orthoformate on dimethyl diketone dissolved in boiling acetic anhydride: 'It is a dark yellow liquid, b. p.  $85-86^\circ/10$  mm.,  $d_4^{15}$  1.0532,  $n_D^{15}$  1.44950,  $n_D^{17}$  1.46601, which solidifies completely at  $-20^\circ$  to a mass of yellow crystals which melts at  $-10^\circ$ . Its vapours have a pronounced olive-green colour. It somewhat readily becomes viscous, and ultimately resinifies when preserved. It is rapidly decomposed by alkali hydroxides, ammonia, and concentrated acids, but the sensitiveness of the substance to these reagents is such that definite products of the change cannot be isolated. When treated with *o*-phenylenediamine in the presence of pyridine, it gives the *quinazoline* deriv-

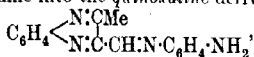
ative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{N}=\text{C}\cdot\text{CH}:\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \end{smallmatrix}$ , leaflets, m. p.  $183^\circ$ .

With aniline in methyl-alcoholic solution, it gives the *anilaniide*, small, colourless needles, m. p.  $187-188^\circ$ , to which the constitution  $\text{NPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CMe}\cdot\text{NPh}$  is ascribed. When treated with phenylhydrazine under very mild conditions, the ethoxymethylene compound yields the *monophenylhydrazone*,  $\text{OEtCH}:\text{CH}\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{NHPh}$ , yellowish-brown rodlets, m. p.  $152^\circ$ , the constitution of which is established by the observation that, under more energetic conditions, a second molecular proportion of phenylhydrazine enters into the reaction, whereby the *pyrazole* derivative,



pale yellow leaflets, m. p.  $182^\circ$ , is formed. The addition of piperidine to a solution of ethoxymethylenediacetyl in light petroleum leads to the formation of the *piperidide*,  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ , lemon-yellow needles, m. p.  $81.5^\circ$ .

Ozonisation of  $\alpha$ -ethoxy- $\Delta^5$ -butene- $\gamma\delta$ -dione dissolved in chloroform and subsequent decomposition of the oily *ozonide* with water leads to the production of  $\alpha\beta$ -diketobutaldehyde,  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CHO}$ ; the compound has not yet been isolated, but its existence is placed beyond doubt by the conversion of the crude material by means of *o*-phenylenediamine into the *quinazoline* derivative,



leaflets, m. p.  $166^\circ$ .

$\alpha$ -Ethoxy- $\Delta^5$ -pentene- $\gamma\delta$ -dione is smoothly hydrogenated in methyl-alcoholic solution in the presence of colloidal palladium to  $\alpha$ -ethoxypentane- $\gamma\delta$ -dione,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}$ , b. p.  $70-73^\circ/13$  mm.,  $d_4^{15}$  1.0690,  $n_D^{15}$  1.43588,  $n_D^{17}$  1.44477, which is much more stable than the corresponding unsaturated compound; the *disemicarbazone*, m. p.  $244^\circ$  (decomp.) after previous darkening, is described.

Attempts have been made to replace dimethyl diketone in the condensation just described by the less expensive methyl ether of its oxime,  $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMe}$ . In this case, however, the use of ethyl orthoformate and acetic anhydride is unsuccessful. The

alternative method of condensation (action of sodium ethoxide and ethyl orthoformate) gives well-defined products in the formation of which the ester does not take a part. The isolation of a substance,  $\text{OMe}\cdot\text{N}\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMe}$ , long, lustrous needles, m. p.  $50^\circ$  (phenylhydrazone,  $\text{C}_{16}\text{H}_{23}\text{O}_2\text{N}_4$ , yellow leaflets, m. p.  $110^\circ$ ), and of a product,  $\text{C}_{10}\text{H}_{16}\text{O}_3\text{N}_2$ , hexagonal leaflets, m. p.  $138.5^\circ$ , is described; the constitution of the latter has not been elucidated. H. W.

**1:3:4:6-Tetramethyl Fructose.** JAMES COLQUHOUN IRVINE and JOCELYN PATTERSON (T., 1922, 121, 2696—2703).

**Structure of Fucose.** E. P. CLARK (J. Biol. Chem., 1922, 54, 65—73).—The method for the preparation of fucose has been improved. Using the methods employed by Hudson and Chernoff (A., 1918, i, 335) in the case of rhamnose, a methyl tetronolactone, m. p.  $110^\circ$ ,  $[\alpha]_D^{20} -63.65^\circ$ , and a methyl tetronamide, m. p.  $112.5^\circ$ ,  $[\alpha]_D^{20} +18.48^\circ$ , have been obtained from fucose. Fuconic acid, when saturated with ammonia in alcoholic solution, yields fuconamide, m. p.  $180.5^\circ$ ,  $[\alpha]_D^{20} -31.13^\circ$ . On the basis of the relationships which exist between the configuration and rotation of lactones and amides of sugar acids (Hudson, A., 1910, i, 220; 1918, i, 293), it is concluded from the above data that the configuration assigned to fucose by Mayer and Tollens (A., 1907, i, 588) is correct. E. S.

**Oxidation of Carbohydrates with Nitric Acid.** PAUL HAAS and BARBARA RUSSELL-WELLS (Biochem. J., 1922, 16, 572—573).—The carbohydrate constituents of *Chondrus crispus*, sucrose, lactose, dextrose, and laevulose, on oxidation with nitric acid, yield a substance similar to glycuronic acid which reduces Fehling's solution in the cold. Attempts to prepare a crystalline oxime, phenylhydrazone, *p*-bromophenylhydrazone, or a cinchonine salt failed. S. S. Z.

**The Oxidation of Sucrose by Nitric Acid.** FREDERICK DANIEL CHATTAWAY and HINTON JOHN HARRIS (T., 1922, 121, 2703—2709).

**Cellulose. III. Determination of the Viscosity of Cellulose.** MICHIMARO NAKANO (J. Chem. Ind. Japan, 1922, 25, 899—910).—The author has studied the preparation of the cuprammonium solution and the effects of various factors on the viscosity of the cuprammonium solution of cellulose, the result being summarised as follows. The viscosity decreases with time until it attains a constant value. A dilute solution attains a constant value more rapidly than a concentrated one, but with a very dilute solution the value is constant from the beginning. With solutions of the same concentration, the lower the viscosity the less is the difference between the final and initial values; the viscosity increases much more rapidly than the concentration. The relative viscosity increases with the temperature. No appreciable decrease of viscosity due to a small loss of ammonia could be observed. Oxygen and light have the largest effect on the viscosity. The depolymerisation of the molecular aggregate of cellulose is due to the

action of light. Of the various preliminary treatments of cellulose, the thermal treatment is the deciding factor for viscosity. K. K.

**Nature of the Swelling Process. VI. Swelling and Partition of Cellulose Acetate in Organic Solvents.** F. KNOEVENAGEL, J. HOGREFE, and F. MERTENS (*Koll. Chem. Beihefte*, 1922, **16**, 180—214; cf. A., 1921, i, 402, 709, 710, 771).—The swelling and partition of cellulose acetate in the mixtures, acetic acid-water, acetic acid-benzene, acetone-benzene, nitrobenzene-*iso*-propyl alcohol, ethyl alcohol-benzene, nitrobenzene-benzene, ethyl alcohol-water, acetic acid-nitrobenzene, acetone-nitrobenzene, methyl alcohol-nitrobenzene, acetone-methyl alcohol, and acetic acid-camphor has been investigated. Cellulose acetate soluble in acetone or chloroform or insoluble in acetic acid was used in the various experiments. The present experiments are an extension of those previously published (*loc. cit.*), and show that alcohols, benzene, and water in varying quantities are taken up by cellulose acetate in constant amounts. In these cases, the law of constant combining proportions is applicable, and it is suggested that where this law holds it is well to speak of compounds and to regard the taking up of the liquids as a chemical process. The compounds involved in these cases are in all probability of a higher order than molecular compounds. The valency involved in these cases is shown to be due to electrical forces. The nature of this type of combination is considered, and it is shown that the swelling process consists of a reaction between two molecules and is of a chemical nature. J. F. S.

**Hydrocellulose.** EMIL HEUSER and WALTER VON NEUENSTEIN (*Cellulosechemie*, 1922, **3**, 89—96).—According to recent theories (Herzog and Jancke, A., 1921, ii, 532; Karrer, A., 1922, i, 231), the cellulose substance is built up of double molecules of anhydrocellobiose, which are systematically arranged in crystal symmetry and held together by special affinities called crystal valencies. These crystal valencies are assumed to be released by all processes which destroy the fibrous structure. The attack on the crystal valencies produces only physical changes, converting the fibrous crystal cellulose into amorphous cellulose, the double anhydrocellobiose molecules remaining intact. The first stage of chemical hydrolysis would involve an attack on the anhydride position of one of the cellobiose residues, without depolymerising the unit, and it is suggested that hydrocellulose is thus formed, consisting of cellobiose-anhydrocellobiose differing from the simple amorphous cellulose as regards the open carbonyl group, but not in molecular dimensions. Further hydrolysis involves the first stage of depolymerisation with formation of free cellobiose, accompanied or closely followed by the second stage, with formation of dextrose. Girard's hydrocellulose produced from fibrous cellulose is a mixture of cellulose and true hydrocellulose, but the hydrocellulose produced by Knoevenagel and Busch's method (A., 1922, i, 636) from viscose cellulose is a homogeneous hydrocellulose, because it is formed from cellulose in which the crystal valencies

have already been resolved. This view is supported by the preparation of highly methylated derivatives by Denham and Woodhouse's method. Ordinary cotton cellulose, on repeated methylation, gave a product corresponding with dimethylcellulose, almost completely insoluble in cold water and in organic solvents. The product from the pure hydrocellulose of Knoevenagel and Busch, with the same methoxyl content, was completely soluble in these media and behaved as a uniform substance. Girard's hydrocellulose yielded a mixed product, partly soluble like that from the pure hydrocellulose and partly insoluble like that from ordinary cotton. In no case was a trimethylated derivative obtained. The dimethylhydrocellulose from Knoevenagel and Busch's product yielded on acetylation principally monoacetyldimethylhydrocellulose soluble in organic solvents and with relatively low melting point. Determinations of molecular weights of these derivatives gave low but inconclusive results.

J. F. B.

**Plant Colloids. XIV. Physico-chemical Analysis of Agar Jellies.** M. SAMEC and V. ISAJEVIĆ (*Koll. Chem. Beihefte*, 1922, **46**, 285—300; cf. A., 1922, i, 921).—Agar-agar is shown to contain a not inconsiderable quantity of electrolytes, which are so closely combined with the organic substances that neither dialysis nor electro-dialysis is sufficient to remove them from the residue of the gum. The chief constituents of agar ash are sulphuric acid and calcium, and a little silicic acid is also present. On boiling the agar solution under pressure, the sulphuric acid passes into an easily dialysable form. Simultaneously with this, the whole of the physico-chemical properties of the solution change, so that a causal connexion between the sulphur content and the power of forming jellies is deduced. Gelose-sulphuric acid is a typical constituent of agar, and in this the sulphuric acid is in all probability present as an ester. The mean molecular weight of this substance is about 9000. It is a monobasic acid and contains one atom of sulphur in each molecule. Agar jellies reach the maximum of their tenacity at the neutral point.

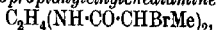
J. F. S.

**Preparation of Aliphatic Dialkylaminoalkyl Compounds.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (*Brit. Pat.* 169185, addition to 167781 (cf. A., 1922, i, 529).—The condensation described in the main patent can be carried out by causing an alkali hydroxide to act on a mixture, in molecular proportions, of a dialkylhalogeno-alkylamine, and a substance of the general formula  $R\cdot CO\cdot CHR'\cdot X$  such as ethyl acetoacetate. Further, a purer product is obtained if the reaction mixture is mixed with benzene and shaken with ammonia before drying and distilling. Ethyl diethylaminoethylacetoacetate, prepared in this way from diethylchloroethylamine and ethyl acetoacetate, boils at 130—132°/10 mm.

G. F. M.

**New Compounds of Diamines. II.** PETER BERGELL (*Z. physiol. Chem.*, 1922, **123**, 280—289).—The following compounds

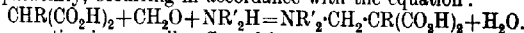
have been prepared from ethylenediamine and the necessary acid chloride:—*di-α-bromopropionylethylenediamine*,



white, glistening needles, m. p. 203°, *dichloroacetylenediamine*, long, rectangular or rhombic prisms, m. p. 171—172°, *di-β-naphthalenesulphonylethylenediamine*, fine needles. From pentamethylenediamine, *di-α-bromopropionylpentamethylenediamine*, and *di-β-naphthalenesulphonylpentamethylenediamine*, m. p. 147°. From these halogenated compounds, on heating with ammonia, the corresponding amino-derivatives are formed, but were not isolated. On treating that obtained from dibromopropionylpentamethylenediamine with β-bromopropionyl bromide, *di-α-bromopropionyl-dialanylethylenediamine*, m. p. 180°, is obtained. W. O. K.

**Dialkylaminoalkyl Compounds.** M. BOCKMÜHL and A. SCHWARZ (U.S. Pat. 1429922).—Ethyl α-(diethylaminoethyl)-acetoacetate, b. p. 132—135°/10 mm., is prepared by mixing 136 parts of diethylaminoethyl chloride with 130 parts of ethyl acetoacetate and gradually stirring into the mixture 57—58 parts of powdered alkali hydroxide, cooling, treating with benzene, shaking the benzene solution with ammonia, drying and distilling. As an alternative method, alkali hydroxide may be gradually introduced into diethylaminoethyl bromide hydrobromide and ethyl acetoacetate. The corresponding α-dimethyl ester, b. p. 124°/12 mm., may be similarly prepared from dimethylaminoethyl chloride. Ethyl diethylaminobutylacetoacetate, b. p. 138°/10 mm., is prepared from diethylaminochlorobutanol, ethyl acetoacetate, and powdered alkali hydroxide. CHEMICAL ABSTRACTS.

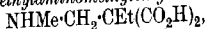
**β-Aminodicarboxylic Acids and Aminopolycarboxylic Acids.** C. MANNICH and ERIC GANZ (*Ber.*, 1922, 55, [B], 3486—3504).—In a previous communication (A., 1920, i, 719), Mannich and Kather have described the preparation of ω-dimethylamino-dimethylmalonic acid from methylmalonic acid, dimethylamine, and formaldehyde. The reaction is now shown to be of general applicability, occurring in accordance with the equation:



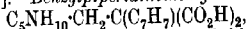
The reaction is generally effected by mixing concentrated solutions of formaldehyde and of a monosubstituted malonic acid which has been half neutralised by the requisite base and preserving the mixture in ice. In general, the new acid separates spontaneously or after addition of alcohol or acetone; if this is not the case, there is little likelihood of a successful preparation owing to the instability of the products. The nature of the substituent introduced into the malonic acid has but little influence on the course of the change, provided that it is aliphatic or fatty aromatic; with aromatic constituents, the primarily formed dicarboxylic acid suffers immediate loss of carbon dioxide. Secondary bases, such as dimethylamine and piperidine, are more suitable than primary bases or ammonia with which frequently more than one hydrogen atom becomes involved in the reaction.

The  $\beta$ -amino-dicarboxylic acids are generally unstable and decompose readily in substance or in solution with the production of  $\alpha$ -substituted acrylic acids. The change is conveniently effected by boiling them in neutral solution. It has not been found possible to discover conditions under which carbon dioxide is evolved without elimination of the basic group. On the other hand, the conversion of the aminodi- into the aminomono-carboxylic acid appears to be possible through the esters, since the dicarboxylic acids when treated with alcoholic hydrogen chloride give esters of the mono-carboxylic acids which can be hydrolysed by aqueous hydrochloric acids to the acid hydrochlorides. The place of the monosubstituted malonic acids may be taken by ethanetricarboxylic acid,  $\text{CH}(\text{CO}_2\text{H})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , but not apparently by ethanetetra-carboxylic or methylenedimalonic acid. Cyanoacetic acid may also be used.

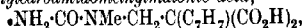
The following substances are described: *Dimethylaminomethyl-ethylmalonic acid*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{H})_2$ , plates, m. p.  $101^\circ$  (decomp.), which is readily decomposed into  $\alpha$ -ethylacrylic acid, b. p.  $179-180^\circ$ . *Methylaminomethylethylmalonic acid*,



m. p. about  $136^\circ$  (decomp.), and its benzoyl derivative, plates, m. p.  $142^\circ$  (decomp.). *Dimethylaminomethylallylmalonic acid*, rhombic plates, m. p.  $85^\circ$  (decomp.), its chloroplatinate and  $\alpha$ -allyl-acrylic acid, b. p.  $76-78^\circ/16$  mm. (the barium, lead, and silver salts are described).  $\delta$ -Phenylpropyl- $\alpha$ -dimethylaminomethylmalonic acid,  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{NMe}_2)(\text{CO}_2\text{H})_2$ , small, colourless needles, m. p. about  $115^\circ$  (decomp.) [from  $\delta$ -phenylpropylmalonic acid, dimethylamine, and formaldehyde], and  $\delta$ -phenyl- $\alpha$ -methyleneglutaric acid,  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2) \cdot \text{CO}_2\text{H}$ , m. p.  $45^\circ$  (silver salt, leaflets). *Benzylidimethylaminomethylmalonic acid*, needles, m. p.  $88^\circ$ , and  $\alpha$ -benzylacrylic acid,  $\text{CH}_2 \cdot \text{C}(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$ , m. p.  $68^\circ$  [the latter acid yields a dibromide,  $\text{CH}_2\text{Ph} \cdot \text{CBr}(\text{CH}_2\text{Br}) \cdot \text{CO}_2\text{H}$ , needles, m. p.  $145^\circ$ ; it is oxidised by potassium permanganate in faintly alkaline solution to  $\alpha$ -benzylglyceric acid,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$ , prisms, m. p.  $127^\circ$ ]. *Benzylpiperidinomethylmalonic acid*,



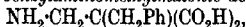
decomp. about  $121^\circ$ , and its sparingly soluble lead and barium salts; the acid is converted by alcoholic hydrogen chloride at the atmospheric temperature into ethyl  $\alpha$ -benzyl- $\beta$ -piperidinopropionate hydrochloride,  $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_5) \cdot \text{CO}_2\text{Et} \cdot \text{HCl}$ , plates, m. p.  $185^\circ$ , which is hydrolysed by concentrated hydrochloric acid to  $\alpha$ -benzyl- $\beta$ -piperidinopropionic acid hydrochloride, small plates, m. p.  $146^\circ$ . *Benzylmethylaminomethylmalonic acid*, small needles, m. p. about  $150^\circ$  (decomp.), its benzoyl derivative, m. p. about  $138^\circ$  (decomp.), and nitroso-compound, plates, m. p. about  $122^\circ$  (decomp.); [the sodium salt of the acid is transformed by potassium cyanate into benzylmethylcarbamidomethylmalonic acid,



small plates, m. p. about  $98^\circ$  (decomp.), which when heated in boiling xylene passes into  $\alpha$ -benzyl- $\beta$ -methylcarbamidopropionic acid,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$ ; the latter substance is converted by boiling acetic anhydride into 2 : 4-diketo-5-benzyl-1-methyl-

hexahydropyrimidine,  $\text{CO} \begin{smallmatrix} \text{NH} - \text{CO} \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{Ph}$ , small needles, m. p. 78°]. Benzylallylaminomethylmalonic acid,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2 \text{Ph})(\text{CO}_2\text{H})_2$ , needles, m. p. 138° (decomp.), and its sparingly soluble lead and barium salts.

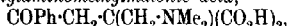
According to experimental conditions, benzylmalonic acid is converted by ammonia and formaldehyde into iminobis-methyl-benzylmalonic acid,  $\text{NH}[\text{CH}_2 \cdot \text{C}(\text{CH}_2 \text{Ph})(\text{CO}_2\text{H})_2]_2$ , small plates, m. p. 107° (decomp.), or benzylaminomethylmalonic acid,



lustrous leaflets, m. p. about 148° (decomp.); either substance is transformed in boiling neutral aqueous solution into  $\alpha$ -benzylacrylic acid.

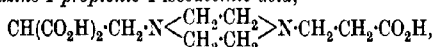
$\beta$ -Dimethylamino- $\alpha$ -phenylpropionic acid,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$ , needles, m. p. 143°, prepared from phenylmalonic acid, dimethylamine, and formaldehyde at 0°, is transformed by being heated into atropic acid, m. p. 106°. Phenylmalonic acid, ammonia, and formaldehyde yield  $\beta$ -amino- $\alpha$ -phenylpropionic acid, which is isolated as the hydrochloride, m. p. 185°; it is converted by phenylacetyl chloride to a small extent into  $\beta$ -phenylacetyl-amino- $\alpha$ -phenylpropionic acid, small needles, m. p. 185°, the main product of the reaction being, however, phenylacetamide. Phenylmalonic acid, ammonium chloride, and formaldehyde give  $\beta$ -iminobis- $\alpha$ -phenylpropionic acid,  $\text{NH}(\text{CH}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{H})_2$ , which is isolated as the hydrochloride, m. p. 112°; it passes into atropic acid when boiled in neutral solution.

Phenacyldimethylaminomethylmalonic acid,

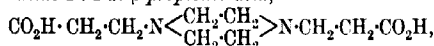


needles, m. p. about 148° (decomp.), and phenacylmethylaminomethylmalonic acid, m. p. 105° (decomp.), are obtained in the usual manner; the sparingly soluble lead and barium salts of the latter acid are mentioned.

Piperazine-1-propionic-4-isosuccinic acid,

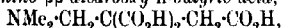


leaflets, m. p. about 227° (decomp.), after becoming discoloured at 200°, is prepared from malonic acid, piperazine, and formaldehyde, and is converted by hot aqueous hydrochloric acid into piperazine-1:4-di- $\beta$ -propionic acid,



which is isolated as the dihydrochloride, m. p. 261–262° (decomp.).

Ethanetricarboxylic acid, dimethylamine, and formaldehyde yield  $\gamma$ -dimethylamino- $\beta\beta$ -dicarboxy-n-butyric acid,



needles, m. p. about 135° (decomp.), which passes in boiling aqueous solution by loss of carbon dioxide into  $\gamma$ -dimethylamino- $\beta$ -carboxy-n-butyric acid,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 158°. The latter acid is transformed into itaconic acid by treatment of its crystalline methiodide with potassium hydroxide.

The action of formaldehyde on dimethylammonium cyanoacetate is accompanied by the evolution of carbon dioxide; the product of the action consists doubtless of  $\beta$ -dimethylaminopropionitrile,  $\text{NMe}_2\text{CH}_2\text{CH}_2\text{CN}$ . Its isolation could not be effected, but its presence is established by the formation of acrylic acid when the crude product is treated with hydrogen chloride.

H. W.

**A Synthesis of Aminohydroxydicarboxylic Acids.** C. MANNICH and M. BAUROTH (*Ber.*, 1922, 55, [B], 3504—3509).—A synthesis of  $\beta$ -aminodicarboxylic acids from monosubstituted malonic acids, formaldehyde, and amines has been described by Mannich and Kather (*A.*, 1920, i, 719) and Mannich and Ganz (preceding abstract). If, under otherwise similar conditions, the alkylmalonic is replaced by tartronic (hydroxymalonic) acid, aminohydroxydicarboxylic acids are produced. These, like the compounds described previously, are unstable substances, and when warmed with water undergo simultaneous decomposition in two directions; thus dimethylaminomethyltartronic acid becomes transformed on the one hand by simple loss of carbon dioxide into  $\beta$ -dimethylamino- $\alpha$ -hydroxypropionic acid, and, on the other, by loss of carbon dioxide and dimethylamine, into pyruvic acid.  $\beta$ -Dimethylamino- $\alpha$ -hydroxypropionic acid is not an intermediate compound in the latter change, since it is stable under the experimental conditions adopted.

*Dimethylaminomethyltartronic acid*,  $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{NMe}_2)(\text{CO}_2\text{H})_2$ , plates, m. p. about  $115^\circ$  (decomp.), is prepared by the action of formaldehyde at  $0^\circ$  on a concentrated aqueous solution of tartronic acid which has been half neutralised by dimethylamine. It yields  $\beta$ -dimethylamino- $\alpha$ -hydroxypropionic acid,  $\text{NMe}_2\text{CH}_2\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , which is analysed in the form of its hydrochloride, rodlets, m. p.  $145$ — $146^\circ$ . *Methylaminomethyltartronic acid*,



aggregates of coarse needles, m. p. about  $153^\circ$  (decomp.), when rapidly heated, is similarly prepared from tartronic acid, formaldehyde, and methylamine and is converted by hot water and hydrochloric acid into  $\beta$ -methylamino- $\alpha$ -hydroxypropionic acid hydrochloride, transparent pyramids, m. p.  $155$ — $156^\circ$ . *Aminomethyltartronic acid*,  $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{NH}_2)(\text{CO}_2\text{H})_2$ , coarse crystals, m. p. about  $138^\circ$  (decomp.), is decomposed by hot water into pyruvic acid in small amount;  $\beta$ -amino- $\alpha$ -hydroxypropionic acid does not appear to be produced. *Piperidinomethyltartronic acid* crystallises in leaflets, m. p. about  $190^\circ$  (decomp.).

H. W.

**The Carbamide Rearrangement.** TENNEY L. DAVIS and H. W. UNDERWOOD, jun. (*J. Amer. Chem. Soc.*, 1922, 44, 2595—2604).—It is shown that carbamide, thiocarbamide, and guanidine and their derivatives undergo the "urea rearrangement." Carbamide yields ammonia and isocyanic acid, and the other compounds yield derivatives of ammonia and of isocyanic acid. Such rearrangement forms the basis of a number of syntheses.  $s$ -Disubstituted aromatic carbamides may conveniently be prepared by

heating carbamide with primary aromatic amines. In the aliphatic series, the reaction succeeds, but the products are more difficult to isolate, and the process is being further studied. The similarity between guanidine and carbamide, and between cyanamide and isocyanic acid in respect to a number of their reactions is pointed out. It is considered that the polymerisation of cyanamide to dicyanodiamide, when its aqueous solution is evaporated, is believed to be a case of the "urea dearrangement."

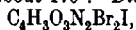
The explanation of the formation of melamine, when aqueous ammonia and dicyanodiamide are heated together, previously given (A., 1922, i, 118), is probably wrong. A portion of the dicyanodiamide is hydrolysed by the action of the ammonia to yield, first, guanylcarbamide and later guanidine, and the latter dearranges to form cyanamide, which combines with the unaltered dicyanodiamide to yield melamine. W. G.

**Trihalogenated Pyvurins.** M. GARINO (*Gazzetta*, 1922, 52, ii, 207—220).—Various compounds analogous to Fischer's tribromopyvurin (A., 1887, 918) have been prepared, pyruvic acid being converted into the dichloro- or dibromo-derivative and this treated with carbamide in presence of sulphuric acid to give the dihalogenated pyvureide, which yields the trihalogenated pyvurin when subjected to the action of a halogen. The stability of these compounds, and also their solubility in water, 95% alcohol, or ether, diminish as the chlorine is replaced by bromine, and no derivative with more than one atom of iodine could be obtained. When treated carefully with dilute alkali solution, the trihalogenated pyvurins yield the corresponding analogues of chloroform, the readiness with which this decomposition occurs increasing as the atomic weight of the halogens present increases. Pharmacological experiments on mammals of various species show that, whereas trichloropyvurin passes almost unchanged through the organism, the tribromo-compound is decomposed with formation of bromoform and produces prolonged narcosis.

*Dichloropyvureide*,  $\text{CCl}_2\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , prepared from dichloropyruvic acid, is a white, pulverulent substance, m. p.  $286^\circ$ , subliming unchanged at about  $170^\circ$ .

*Trichloropyvurin*,  $\text{CCl}_3\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises in soft, lustrous plates, m. p.  $242^\circ$  (decomp.), and gives the phenylcarbylamine reaction with potassium hydroxide and aniline; with potassium hydroxide and  $\beta$ -naphthol it gives a greenish-blue coloration and with thymol a reddish-violet coloration. It readily forms supersaturated solutions in water.

*Dichlorobromopyvurin*,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_2\text{Cl}_2\text{Br}$ , forms lustrous, white scales, m. p.  $236^\circ$  (decomp.). *Chlorodibromopyvurin*,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_2\text{ClBr}_2$ , forms white, lamellar crystals, m. p.  $238^\circ$  (decomp.). *Dichloriodopyvurin*,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_2\text{Cl}_2\text{I}$ , forms yellow crystals, m. p. about  $230^\circ$  (decomp.), and begins to yield iodine vapour at about  $150^\circ$  or, if very slowly heated, at about  $170^\circ$ . *Dibromiodopyvurin*,



forms white crystals turning yellow in the light, m. p.  $197^{\circ}$  (decomp.), and begins to emit iodine at about  $105^{\circ}$ . T. H. P.

**Preparation of Chlorobromoiodypyurin.** M. GARINO and I. MUZIO (*Gazzetta*, 1922, 52, ii, 226—232).—Chloropyruvic acid (cf. Genvresse, *Bull. Soc. chim.*, 1892, [iii], 7, 83), prepared by the action of sulphuryl chloride on pyruvic acid, forms white, rhombohedral crystals ( $+H_2O$ ), m. p.  $55^{\circ}$ , and decomposes between  $122^{\circ}$  and  $155^{\circ}$ ; the anhydrous acid, m. p. about  $45^{\circ}$ , is very unstable. Chlorobromopyruvic acid,  $CHClBr\cdot CO\cdot CO_2H$ , forms white, tabular crystals, m. p.  $105^{\circ}$ .

Chlorobromopyruvide,  $CClBr\cdot C \begin{smallmatrix} < NH\cdot CO \\ CO\cdot NH \end{smallmatrix}$ , forms a light, white precipitate, and begins to sublime at about  $120^{\circ}$ . Chlorobromoiodypyurin,  $CClBr\cdot CO\cdot CO\cdot NH\cdot CO\cdot NH_2$ , prepared by treating the preceding compound with iodine in presence of iodic acid and carbon tetrachloride, forms white crystals, m. p.  $233^{\circ}$  (decomp.), and begins to emit iodine at  $160^{\circ}$ . It is highly stable in the dry state, but readily decomposes in solution, especially under the influence of light. In presence of potassium hydroxide, it gives a violet coloration with thymol and a blue coloration with  $\beta$ -naphthol; with potassium hydroxide and aniline, it forms phenylcarbylamine. When treated with potassium hydroxide under certain conditions, it yields ammonium oxalurate and chlorobromiodomethane, which is being investigated further. T. H. P.

**Electrolytic Dissociation of Dicyanodiamide in Aqueous Solution.** NAOTO KAMEYAMA (*J. Coll. Eng. Tokyo*, 1922, 11, 185—191).—By measuring the conductivity of solutions of sodium hydroxide and dicyanodiamide at  $25^{\circ}$ , the hydrolysis of sodium dicyanodiamide in 0.1 mol. solution was found to be 94.5%. In more dilute solutions, hydrolysis is almost complete. The dissociation constant at  $25^{\circ}$  is  $0.6 \times 10^{-14}$ . The basic properties of dicyanodiamide are very feeble, the hydrochloride, if it exists at all, being completely hydrolysed in aqueous solution. G. F. M.

**Attempts to Prepare Carbonyl Cyanide and a Method of Obtaining Unsaturated Amino-acids.** OTTO DIELS, HUGO GÄRTNER, and RICHARD KAACK (*Ber.*, 1922, 55, [B], 3439—3448).—Attempts are described to prepare carbonyl cyanide,  $CO(CN)_2$ , by the ozonisation of suitable derivatives of malononitrile; these, however, have not been completely successful. A synthesis of unsaturated amino-acids from ethyl cyanoethoxyacrylate has been effected.

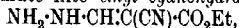
Ethoxymethylenemalononitrile,  $OEt\cdot CH\cdot C(CN)_2$ , large, colourless crystals, m. p.  $65$ — $66^{\circ}$  after previous softening, is prepared by the protracted heating of a solution of malononitrile and ethyl orthoformate in acetic anhydride. It is converted by boiling water into hydroxymethylenemalononitrile, m. p.  $135^{\circ}$  (decomp.) [hydrochloride,  $C_4H_5ON_2Cl$ , lustrous needles, m. p.  $221^{\circ}$  (decomp.)], and by ammonia (25%) into aminomethylenemalononitrile, pale yellow crystals, m. p.

146°. Ozonisation of ethoxymethylenemalononitrile dissolved in glacial acetic acid under varied conditions of temperature and concentration has not led to conclusive results, but, in certain circumstances, a crystalline material has been isolated in very small amount, the properties of which are such as might be expected to be shown by carbonyl cyanide. Ozonisation of ethyl cyanoethoxyacrylate dissolved in ethyl acetate leads to the production of an ozonide which is decomposed by warm water with formation of oxalic acid. Benzylidenemalononitrile is unexpectedly resistant towards the action of ozone.

Malononitrile reacts energetically with acetaldehyde at 0° in the presence of a drop of piperidine, and gives 1:3-dimethylcyclobutane-2:2:4:4-tetranitrile,  $(\text{CN})_2\text{C} \begin{smallmatrix} < \text{CHMe} \\ < \text{CHMe} \end{smallmatrix} > \text{C}(\text{CN})_2$ , small, colourless needles, m. p. 184—185°. In the presence of ethyl alcohol, the same substances yield ethylidenebismalononitrile,  $\text{HMe}[\text{CH}(\text{CN})_2]_2$ , colourless, prismatic crystals, m. p. 113—114°, which is decomposed by warm water with formation of acetaldehyde. Methylenebismalononitrile, large prisms, m. p. 136—137°, is prepared by the action of formaldehyde (40%) on a solution of malononitrile in alcohol. It dissolves in boiling water to a clear solution from which spindle-like crystals, m. p. about 192—195° after darkening at about 130°, separate; the filtrate from these crystals, if again boiled for a short time, deposits lustrous leaflets, m. p. 231—233° after darkening at about 200°. The composition of the two compounds is identical, but their further investigation has not been possible owing to lack of material.

Ethyl ethoxymethylenecyanoacetate is converted by benzylamine in ethyl-alcoholic (95%) solution into ethyl  $\alpha$ -cyano- $\beta$ -benzylaminoacrylate,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , thick, colourless needles, m. p. 103—104°, which is slowly transformed by a solution of sodium in boiling ethyl alcohol (96%) into  $\beta$ -benzylaminoacrylic acid,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , colourless, unctuous leaflets, m. p. 97—98°, b. p. 105—106°/12 mm. (the sodium and silver salts are described).  $\beta$ -Anilinoacrylic acid, m. p. 156°, is prepared similarly and in poor yield from ethyl cyanoanilinoacrylate.

Ethyl cyanoethoxyacrylate is converted by cautious treatment with hydrazine hydrate into ethyl cyanohydrazinoacrylate,



slender, colourless needles, m. p. 96—97°, which, with acetone, yields the compound,  $\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , rhombohedra, m. p. 78—79°.

H. W.

**Possible Asymmetry of Aliphatic Diazo-compounds. III.**  
P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1922, 54, 101—103).—When fused with benzoic acid, ethyl diazosuccinate yields ethyl benzoylmalate, b. p. 147—148°/3 mm., 143°/2 mm. The products from two preparations had  $[\alpha]_D^{25} +0.22^\circ$  and  $+0.12^\circ$ , respectively. The authors regard the rotations obtained as additional evidence of the existence of optically active diazosuccinic esters (cf. A., 1922, i, 818).

E. S.

***s*-Diisopropylhydrazine and its Derivatives. II. HARRY L. LOCHTE, WILLIAM A. NOYES, and JAMES R. BAILEY (*J. Amer. Chem. Soc.*, 1922, **44**, 2556—2567; cf. A., 1922, i, 329).—*s*-Di-**

**isopropylhydrazine** has been carefully purified and some of its physical constants have been redetermined with the following results: b. p. 124.5°/750 mm.,  $d_4^{20}$  0.7844,  $n_D^{20}$  1.4125. It gives an *oxalate*, m. p. 200°, and a *semicarbazide* derivative, m. p. 100°. If the dry hydrochloride is mixed with a 30% excess of dry powdered copper oxide in a stoppered flask and after a week the mixture is distilled, 2:2'-azopropane, b. p. 88.5°/750 mm.,  $d_4^{20}$  0.7408,  $n_D^{20}$  1.3890, is obtained. This compound is readily reduced to the symmetrical hydrazine, but weak oxidising agents have no effect on it. When left in contact with solid sodium or potassium hydroxides, it is partly converted into acetoneisopropylhydrazone.

*iso*Propylhydrazine,  $\text{CHMe}_2\text{NH}\cdot\text{NH}_2$ , b. p. 106—107°/750 mm., may be prepared by one of four methods, namely, hydrolysis of the *azo*-derivative, hydrolysis of acetoneisopropylhydrazone, direct reduction of an equimolecular mixture of acetone, hydrazine hydrate, and hydrochloric acid, or by hydrolysis of *isopropylsemicarbazide*. The third method, that of catalytic reduction, as in the case of the *s*-hydrazine, is the most practical one. The base is very unstable and is best isolated as its *hydrochloride*, m. p. 114°, and gives a *dibenzoyl* derivative, m. p. 161.5°, and a *phenylthiosemicarbazide*, m. p. 141.5°. When the free base is mixed with an equimolecular amount of dry acetone and an equal volume of absolute alcohol is added *acetoneisopropylhydrazone*, b. p. 132—134°,  $d_4^{20}$  0.8225,  $n_D^{20}$  1.4360, is obtained.

The *mononitroso*-derivative, b. p. 65—66°/6—8 mm.,  $d_4^{20}$  0.9440,  $n_D^{20}$  1.4420, of *s*-diisopropylhydrazine has been isolated and its sodium salt prepared.

It is suggested that some of the above methods may serve for the preparation of a number of *s*-secondary hydrazines, azoparaffins, monoalkylhydrazines, and mixed hydrazo- and azo-paraffins.

W. G.

**A New Method for the Introduction of an Ethyl Group. The Reaction between Organomagnesium Haloids and Ethyl Sulphate.** HENRY GILMAN and RACHEL E. HOYLE (*J. Amer. Chem. Soc.*, 1922, **44**, 2621—2626).—Ethyl sulphate reacts with organomagnesium haloids in which the group  $\text{MgX}$  is attached to carbon, oxygen, or nitrogen, and in all the cases examined this group was replaced by the ethyl group. The yields of the reaction in a number of cases were decidedly good, and the process should be of value, not only in synthetic chemistry, but also as a trustworthy method for the determination of the mechanism of certain reactions.

W. G.

**The Preparation and Properties of Trimethylstannane.** CHARLES A. KRAUS and WILLARD N. GREER (*J. Amer. Chem. Soc.*, 1922, **44**, 2629—2633).—Metallic sodium acts on trimethylstannic chloride in solution in liquid ammonia to give *sodium trimethylstannide*,  $\text{SnMe}_3\text{Na}$ , and this in turn is decomposed by ammonium

nitrate or chloride in the same solvent to give *trimethylstannane*,  $\text{SnMe}_3\text{H}$ , an oily liquid, b. p.  $60^\circ/750.3$  mm. The stannane is converted by the action of sodium in liquid ammonia to sodium trimethylstannide and with hydrochloric acid in aqueous solution it gives trimethylstannic chloride and hydrogen. W. G.

**The Mutual Influence of Substituents in Poly-substituted Benzenes.** E. KLEUCKER (*Ber.*, 1922, 55, [B], 2941).—The conclusion to which the author has been led that the mutual influence of substituents in ortho- and para-disubstituted benzenes is explicable in the same manner as that between groups at the ends of open-chain, conjugated unsaturated compounds (*A.*, 1922, i, 734) has been reached previously by Angeli (*Atti R. Accad. Lincei*, 1921, [v], 30, ii, 344), whose communication at the time of the author's work was not generally available. H. W.

**Equilibrium in the System *m*-Dinitrobenzene-Urethane.** NICOLAI ANTONOVICH PUSHIN and ALEXANDRA FIOLETOVA (*T.*, 1922, 121, 2822—2823).

**The Action of Thionyl Chloride on Substituted Benzene-sulphonyl Chlorides.** J. POLLAK and ZOSIA RUDICH (*Monatsh.*, 1922, 43, 209—224).—By the action of thionyl chloride on *m*-xylene-2:4-disulphonyl chloride, Pollak and Schadler obtained a substance which appeared to be 2:4-dichloro-*m*-phthaloyl chloride (*A.*, 1918, i, 497). To investigate this type of reaction further, the action of thionyl chloride on *o*- and *p*-toluenesulphonyl chlorides has now been studied. At  $200^\circ$ , *p*-toluenesulphonyl chloride is converted into *p*-chlorobenzylidene chloride, and at  $240^\circ$  almost quantitatively into *p*-chlorobenzoyl chloride; *o*-toluenesulphonyl chloride was converted into *o*-chlorobenzoyl chloride at  $240$ — $250^\circ$ , but under no conditions was *o*-chlorobenzylidene chloride formed. The possibility that chlorobenzotrichlorides are first formed and then hydrolysed by adventitious moisture is shown to be excluded. Toluene itself, on the other hand, gives benzotrichloride and no benzylidene chloride when heated in a sealed tube with thionyl chloride. By the action of thionyl chloride on *o*-xylene-4:6-disulphonyl chloride at  $250^\circ$ , a compound,  $\text{C}_8\text{H}_4\text{Cl}_6$ , m. p.  $78^\circ$ , was obtained, which may be a dichlorodi(dichloromethyl)benzene. At  $320^\circ$ , a crystalline compound, m. p.  $193$ — $196^\circ$ , was formed, which may be a more highly chlorinated derivative of *o*-xylene.

The dichloroisophthalic acid obtained by Pollak and Schadler by the action of thionyl chloride on *m*-xylene-2:4-disulphonyl chloride has been further investigated and found to be 2:6-dichloroisophthalic acid; its *methyl* ester has m. p.  $97$ — $98^\circ$ . The reaction appears, therefore, not to consist simply in replacement of chlorosulphonyl groups by chlorine, but a further rearrangement of the substituting groups is involved. At  $260^\circ$ , *m*-xylene-2:4-disulphonyl chloride is converted by thionyl chloride into a compound,  $\text{C}_8\text{H}_2\text{Cl}_8$ , m. p.  $113$ — $114^\circ$ , and at  $320^\circ$  into a still more highly chlorinated product.

*p*-Anisolesulphonyl chloride reacts with thionyl chloride at  $250^\circ$

to give a compound,  $C_7H_2OCl_6$ , m. p.  $214^\circ$ , probably *chloromethoxy-pentachlorobenzene*.  
E. H. R.

**Esters of the Hydroxyalkylarylamines. I. Acid Sulphuric Esters of the Simple Monohydroxyethylarylamines.** KENNETH HERBERT SAUNDERS (T., 1922, 121, 2667—2675).

**p-Cymene. IV. The Chlorination of 2-Amino-p-cymene.** ALVIN S. WHEELER and I. V. GILES (J. Amer. Chem. Soc., 1922, 44, 2605—2612; cf. A., 1919, i, 490; 1920, i, 751; 1922, i, 332).—When 2-acetamido-p-cymene is chlorinated in solution in carbon tetrachloride 5-chloro-2-acetylamido-p-cymene, m. p.  $109-111^\circ$ , is obtained and on hydrolysis yields 5-chloro-2-amino-p-cymene, b. p.  $240-250^\circ$ , from which the *hydrochloride*, the *sulphate*, and the *benzoyl* derivative, m. p.  $137.5^\circ$ , are prepared. When the hydrochloride is diazotised and the diazo-compound boiled with water, 5-chlorocarvacrol, b. p.  $158/52$  mm., is obtained, and when the diazo-compound is treated with cuprous cyanide in an excess of potassium cyanide and the resulting nitrile hydrolysed, it yields 4-chloro-2-methyl-5-isopropylbenzoic acid, m. p.  $125^\circ$ . When the hydrochloride is diazotised with half the equivalent amount of sodium nitrite, 2 : 2'-diazamino-5 : 5'-dichloro-p-cymene, m. p.  $135-137^\circ$ , is obtained.

The diazotised base couples readily with hydroxy-compounds. The resulting azo-dyes, in which a sulphonic group is present, act as direct dyes when employed in weak acetic acid solution. The others are developed dyes. The colours produced on wool and silk are fast to light and washing. The brilliancy of some is striking, and is undoubtedly due to the presence of the chlorine atom. The following are described. 4(5'-Chlorocarvacrylazo)phenol, m. p.  $196^\circ$ ; 4(5'-chlorocarvacrylazo)resorcinol, m. p.  $188^\circ$  (decomp.); 4(5'-chlorocarvacrylazo)salicylic acid, m. p.  $165^\circ$ , and its sodium salt; 4(5'-chlorocarvacrylazo)- $\alpha$ -naphthol, m. p.  $128^\circ$  (decomp.); 1(5'-chlorocarvacrylazo)- $\beta$ -naphthol, m. p.  $163^\circ$ ; 4(5'-chlorocarvacrylazo)-1-naphthol-2-sulphonic acid and its sodium salt; 2(5'-chlorocarvacrylazo)-1-naphthol-4-sulphonic acid, m. p.  $246^\circ$ , and its sodium salt; 1(5'-chlorocarvacrylazo)-2-naphthol-7-sulphonic acid, m. p.  $228^\circ$  (decomp.).

The constitution of the chloroaminocymene was proved as follows. The chloroacetamidocymene was oxidised by means of potassium permanganate in the presence of magnesium sulphate and yielded 5-chloro-2-acetamido-4-isopropylbenzoic acid, m. p.  $207-209^\circ$ , and this on hydrolysis gave 5-chloro-2-amino-4-isopropylbenzoic acid, m. p.  $159^\circ$ , giving a *hydrochloride*, m. p.  $178^\circ$ . Finally chloroaminocymene was diazotised and the product, by means of the Sandmeyer reaction, was converted into a dichloro-p-cymene, which, on oxidation in a sealed tube with nitric acid at  $180^\circ$  for ten hours, yielded 2 : 5-dichloroterephthalic acid, m. p.  $305^\circ$ .

W. G.

**$\alpha$ -Naphthylnitroamine and its Transformations.** E. BAMBERGER (Ber., 1922, 55, [B], 3383—3392).— $\alpha$ -Naphthylnitroamine differs from other members of this group, which do not contain a

chromophoric group and are colourless, in having a yellow colour. It is converted in a normal manner by mineral acids into 2-nitro- $\alpha$ -naphthylamine, but in alkaline solution it is transformed in an unusual manner into  $\beta$ -naphthaquinone- $\alpha$ -diazide, the reaction probably following the course:  $C_{10}H_7 \cdot NH \cdot NO \rightarrow C_{10}H_7 \cdot N \cdot NO \cdot OH \rightarrow C_6H_4 \cdot \begin{matrix} C(N_2 \cdot OH) \cdot C \cdot OH \\ | \\ CH=CH \end{matrix} \rightarrow C_6H_4 \cdot \begin{matrix} C(N_2) \cdot CO \\ | \\ CH=CH \end{matrix}$ . The peculiar behaviour of  $\alpha$ -naphthylnitroamine probably depends on the feebly acidic nature of its isonitroso-form, and its consequent ready formation by the hydrolysis of its salts and subsequent isomerisation to the quinonediazide.

[With LEO SCHLEIN.]—The conversion of  $\alpha$ -naphthylamine by successive diazotisation and oxidation with potassium ferricyanide into  $\alpha$ -naphthylnitroamine (cf. *Diss. Zürich*, 1894) is described in detail; the substance forms golden-yellow crystals, m. p. 123–124° when rapidly heated. The ammonium, lead, silver, calcium, and barium salts were prepared. The nitroamine is converted by sodium methoxide and methyl iodide into  $\alpha$ -naphthyl-N-methylnitroamine,  $C_{10}H_7 \cdot NMe \cdot NO_2$ , almost colourless, vitreous crystals, m. p. 54.5–55°.

$\alpha$ -Naphthylnitroamine is transformed by aqueous potassium hydroxide at the atmospheric temperature into  $\beta$ -naphthaquinone- $\alpha$ -diazide [ $\beta$ -hydroxy- $\alpha$ -diazonaphthalene], golden-yellow needles, m. p. 94–94.5°; preliminary experiments appear to show that a similar change does not take place with  $\beta$ -naphthylnitroamine.

Reduction of  $\alpha$ -naphthylnitroamine by sodium amalgam and water leads to the formation of naphthalene,  $\alpha$ -naphthylamine,  $\beta$ -naphthol, and ammonia. The production of  $\beta$ - (instead of  $\alpha$ -) naphthol is explained by the established relationship of  $\alpha$ -naphthylnitroamine to  $\beta$ -naphthaquinone- $\alpha$ -diazide.

$\alpha$ -Naphthylnitroamine is converted by nitrous acid in the presence of glacial acetic acid and subsequent treatment with an alkaline solution of  $\beta$ -naphthol into  $\alpha$ -naphthylazo- $\beta$ -naphthol, m. p. 228–229°.

H. W.

**The Mechanism of the Bromination of Phenol in Aqueous Solution.** HARRY BAINES (T., 1922, 121, 2810–2813).

**Reduction of Polynitrophenols by Hydrogen Sulphide in Presence of Ammonia.** L. CHAS. RAIFORD (*Science*, 1921, 53, 218; cf. A., 1920, i, 156).—Reduction of 2:4-dinitrophenol by hydrogen sulphide and ammonia results, in contradiction of previous statements, in the production of isomeric substances. A. A. E.

**Methyl Sulphites of Secondary Aromatic Aliphatic Amines.** M. BOCKMÜHL and K. WINDISCH (U.S. Pat. 1426348).—*Sodium N-ethoxyphenylmethylaminomethyl sulphite*, m. p. 265°, is prepared by heating a mixture of formaldehyde solution, sodium hydrogen sulphite solution, *N*-methylphenetidine, and ethyl alcohol, collecting the product, and redissolving it in dilute ethyl alcohol. The corresponding ethyl derivative is similarly obtained from ethylphenetidine. *Sodium 1-phenyl-2:3-dimethylpyrazol-5-one-4-ethylaminomethyl sulphite*, m. p. (in water of crystallisation) 80–90°, is obtained by

adding a hot solution produced by the interaction of formaldehyde and sodium hydrogen sulphite to ethylaminoantipyrine, concentrating the solution in a vacuum, and purifying with aqueous acetone.

CHEMICAL ABSTRACTS.

**Researches on Residual Affinity and Co-ordination. XII. Cobaltammine and Ferric Lakes of Dinitrosoresorcinol.** GILBERT T. MORGAN and JOHN EWART MOSS (T., 1922, 121, 2857—2866).

**Preparation of New Guaiacol Compounds.** PHARM. AZEUTISCHE INDUSTRIE G. M. B. H. and RUDOLF HAUSCHKA (Austrian Pat. 86131; from *Chem. Zentr.*, 1922, iv, 710).—Silicon tetrachloride or other reactive silicon compound is allowed to react with guaiacol. From silicon tetrachloride and guaiacol, *dichlorodiguaiacysilicomethane*,  $\text{SiCl}_2(\text{O}-\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , and *tetraguaiacysilicomethane*,  $\text{Si}(\text{O}-\text{C}_6\text{H}_4\cdot\text{OMe})_4$ , are obtained, and can be partly separated by distillation in a vacuum. The former is a viscid substance, but by solution in ether and evaporation can be obtained in colourless or greyish-green crystals; it is slowly decomposed by water with separation of silicic acid. The latter is a viscid liquid which by long heating in a vacuum gives off guaiacol vapour and forms *polyguaiacysilicon*,  $\text{Si}_{10}(\text{O}-\text{C}_6\text{H}_4\cdot\text{OMe})_{22}$ , a thick, honey-like syrup, b. p.  $220^\circ/20$  mm. G. W. R.

**Action of Aromatic Alcohols on Phenols in the Presence of Aluminium Chloride.** RALPH C. HUSTON (*Science*, 1920, 52, 206—207).—At relatively low temperatures, benzyl alcohol reacts with phenol in presence of aluminium chloride, giving a 40—50% yield of *p*-benzylphenol. The corresponding methyl and ethyl ethers were obtained in slightly better yields. A. A. E.

**Synthesis of certain Primary Alcohols from Unimolecular Formaldehyde and Grignard's Reagents.** KARL ZIEGLER and PAUL TIEMANN (*Ber.*, 1922, 55, [B], 3406—3416).—An extension of previous work (cf. A., 1921, i, 394).—An ethereal solution of 4-bromo-1-methylnaphthalene is treated successively with activated magnesium powder and gaseous formaldehyde whereby it is transformed into 1-methyl-4-hydroxymethylnaphthalene, small, colourless needles, m. p.  $74\text{--}75^\circ$  (*phenylurethane*, needles, m. p.  $103^\circ$ ); the yield is 40—50% of that theoretically possible, and is greatly dependent on the quality of the magnesium powder. The carbinol is oxidised by the necessary amount of dichromate and sulphuric acid to 1-methylnaphthalene-4-aldehyde, colourless needles, m. p.  $33\text{--}34^\circ$  (the corresponding bisulphite compound, semicarbazone, colourless leaflets, m. p.  $228^\circ$ , and azine, pale yellow crystals, m. p.  $166\text{--}167^\circ$ , are described). 1-Bromo-2-methylnaphthalene is transformed in a similar manner into 2-methyl-1-hydroxymethylnaphthalene, m. p.  $126\text{--}127^\circ$ , in 57% yield (*phenylurethane*, m. p.  $127\text{--}128^\circ$ ). The oxidation of the carbinol to the corresponding aldehyde could not be effected, a part of the original substance being completely burnt, whereas the residue remained unchanged. A solution of

the carbinol in glacial acetic acid is converted by hydrogen chloride and hydrogen bromide, respectively, into 2-methyl-1-chloromethyl-naphthalene, plates, m. p. 61—63°, and 2-methyl-1-bromomethyl-naphthalene, long needles, m. p. 87·5—89°. Reduction by sodium of the latter substance dissolved in moist ether gives 1:2-dimethyl-tetrahydronaphthalene, b. p. 123·5—124·5°/11 mm.,  $d_4^{20}$  0·9847,  $d_4^{25}$  0·9844,  $d_4^{30}$  0·988,  $n_D^{20}$  1·55298,  $n_D^{25}$  1·55762,  $n_D^{30}$  1·57082,  $n_D^{35}$  1·58195,  $n_D^{40}$  1·5593, which appears to contain a small proportion of the dihydro-compound.

$\beta\beta$ -Diphenylvinyl bromide, magnesium, and formaldehyde give  $\gamma$ -phenylcinnamyl ( $\gamma$ -diphenylallyl) alcohol,  $\text{CPh}_2\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ , which is isolated through the corresponding hydrogen phthalate (the sodium salt of the latter is described). The alcohol has m. p. 61·5—63°, b. p. 205°/15 mm., 192°/10 mm. The corresponding acetate has b. p. 205°/15 mm., m. p. 36—37·5°,  $d_4^{20}$  1·1003,  $d_4^{25}$  1·1005,  $d_4^{30}$  1·091,  $n_D^{20}$  1·57980,  $n_D^{25}$  1·58592,  $n_D^{30}$  1·60189,  $n_D^{35}$  1·61734,  $n_D^{40}$  1·5817, whereas the benzoate has m. p. 89—90°. The alcohol is reduced by sodium and ethyl alcohol to  $\alpha\alpha$ -diphenylpropane, b. p. 140—141°/13 mm., 280°/760 mm.,  $d_4^{20}$  0·9951,  $d_4^{25}$  0·990,  $n_D^{20}$  1·56810,  $n_D^{25}$  1·5605. It is converted by hydrogen bromide in glacial acetic acid solution into  $\gamma$ -diphenylallyl bromide,  $\text{CPh}_2\text{CH}\cdot\text{CH}_2\text{Br}$ , m. p. 37—39°, which is transformed into  $\gamma$ -phenylcinnamaldehyde (semicarbazone, m. p. 214—215°).  $\gamma$ -Phenyl- $\beta$ -methylcinnamyl alcohol,  $[\text{CPh}_2\text{CMe}\cdot\text{CH}_2\cdot\text{OH}]$ , crystallises in coarse prisms, m. p. 68—69°, b. p. 184°/11 mm. (benzoate, colourless crystals, m. p. 116°). It is converted by concentrated sulphuric acid in the presence of glacial acetic acid into 1-phenyl-2-methylindene, m. p. 56·5°, its ability to suffer ring closure in this manner being in striking contrast to that of the lower homologue.

$p$ -Dibromobenzene is converted by magnesium and formaldehyde into  $p$ -bromobenzyl alcohol which is readily oxidised to  $p$ -bromobenzaldehyde, m. p. 57°, b. p. 105—110°/12 mm. The latter substance is transformed by magnesium methyl bromide into  $p$ -bromophenyl-methylcarbinol,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHMe}\cdot\text{OH}$ , a colourless, viscous liquid, b. p. 133—134°/15 mm., 127—128°/11 mm.,  $d_4^{20}$  1·4690,  $d_4^{25}$  1·463,  $n_D^{20}$  1·56713,  $n_D^{25}$  1·57190,  $n_D^{30}$  1·58619,  $n_D^{35}$  1·59650,  $n_D^{40}$  1·5697. (The substance can also be prepared from magnesium  $p$ -bromophenyl bromide and acetaldehyde.) It is transformed by sodium hydrogen sulphate at 150° into  $p$ -bromostyrene,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}\cdot\text{CH}_2$ , a colourless, mobile liquid, b. p. 88·5—89·5°/16 mm., 83·5—84·5°/11 mm., m. p. 4·5°,  $d_4^{20}$  1·4098,  $d_4^{25}$  1·401,  $n_D^{20}$  1·59137,  $n_D^{25}$  1·59931,  $n_D^{30}$  1·61960,  $n_D^{35}$  1·63801,  $n_D^{40}$  1·5961.  $p$ -Bromobenzaldehyde and magnesium ethyl bromide give  $p$ -bromophenylethylcarbinol, b. p. 138—139°/11 mm.,  $d_4^{20}$  1·4085,  $d_4^{25}$  1·4084,  $d_4^{30}$  1·404,  $n_D^{20}$  1·55779,  $n_D^{25}$  1·56227,  $n_D^{30}$  1·57505,  $n_D^{35}$  1·58577,  $n_D^{40}$  1·5607, which is converted by sodium hydrogen sulphate into  $p$ -bromopropenylbenzene,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}\cdot\text{CHMe}$ , m. p. 35°, b. p. 108—110°/11 mm., 238—239°/atmospheric pressure,  $d_4^{20}$  1·3309,  $d_4^{25}$  1·356,  $n_D^{20}$  1·57746,  $n_D^{25}$  1·58391,  $n_D^{30}$  1·60372,  $n_D^{35}$  1·62159,  $n_D^{40}$  1·5934. Magnesium  $p$ -bromophenyl bromide and acetone give the expected carbinol, which was

not isolated in the homogeneous condition; it is transformed into *p*-bromoisopropenylbenzene,  $C_6H_4Br-CMe:CH_2$ , b. p.  $110^\circ/11$  mm.  $228^\circ/\text{atmospheric pressure}$ , m. p.  $11^\circ$ ,  $d_4^{20}$  1.3592,  $d_4^{25}$  1.350,  $n_D^{20}$  1.57721,  $n_D^{25}$  1.58346,  $n_D^{30}$  1.60497,  $n_D^{35}$  1.62089,  $n_D^{40}$  1.5835.

The brominated styrenes could only be caused to react incompletely with magnesium. H. W.

**Some Condensation Reactions with Di-*p*-dimethylaminobenzhydrol (Michler's Hydrol).** MARSTON TAYLOR BOGER and A. RUDERMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2612—2621).—Di-*p*-dimethylaminobenzhydrol (Michler's hydrol) condenses with the imides of succinic and phthalic acids to give the corresponding leucauramines, which on hydrolysis by alkali give the amic acids. The condensation may be carried out in either alcoholic solution or concentrated sulphuric acid. Under these conditions, succinimide gives *succinyl-leucauramine*, m. p.  $151^\circ$  (corr.). With nitrous acid, this yields *succinyl-dinitroleucauramine*, m. p.  $94-96^\circ$  (decomp.), and on hydrolysis gives *di-p-dimethylaminobenzhydrysuccinamic acid*, m. p.  $170^\circ$ . Phthalimide and Michler's hydrol give in alcoholic solution *phthalyl-leucauramine* in its stable form, m. p.  $186.7^\circ$  (corr.), whilst, if the condensation takes place in concentrated sulphuric acid, a labile form, m. p.  $90^\circ$ , is obtained and on heating is converted into the stable form. When oxidised with lead peroxide this compound gives *phthalyl-leucauraminocarbinol*, m. p.  $176^\circ$  (corr.). *Dinitrophthalyl-leucauramine*, m. p.  $104^\circ$  (decomp.), and *di-p-dimethylaminobenzhydrylphthalamic acid*, m. p.  $163.8^\circ$  (decomp., corr.), were prepared. The amic acid when oxidised by lead peroxide gave the corresponding *carbinol*, m. p.  $187^\circ$  (corr.). Michler's hydrol did not condense with phthalimidine, but with phthalide gave *di-bis-dimethylaminobenzhydrylphthalide*, m. p.  $201^\circ$  (corr.). A condensation product was not obtained from 4-nitrophthalimide, but 3-aminophthalimide yielded *3-leucauraminylphthalyl-leucauramine*, m. p.  $219-220^\circ$  (corr.).

Anthraquinone, its  $\alpha$ - or  $\beta$ -amino-derivatives, alizarin, thiocarbamide, or benzoylenecarbamide failed to react with the hydrol under the experimental conditions, but dehydrothio-*p*-toluidine condensed readily with the hydrol in alcoholic solution to give *2-di-p-dimethylaminobenzhydrylbenzthiazole*, m. p.  $190-191^\circ$  (corr.).

In alcoholic solution, "saccharin" gives a deep blue coloration with the hydrol even in dilute solution, and this reaction appears to be a delicate test for either compound. W. G.

**Solubility. VII. The Solubility of Salts of Aromatic Acids.** FRITZ EPHRAIM (*Ber.*, 1922, **55**, [B], 3472—3486; cf. A., 1922, ii, 574, and earlier abstracts).—The communication is the first of a series devoted to a study of the solubilities of metallic salts of organic acids and is confined to a qualitative survey of the field. Aqueous solutions of the sodium salts of seventy-three carboxylic or sulphonic acids, generally normal in concentration, are mixed at the atmospheric temperature with equivalent quantities of normal solutions of barium, strontium, calcium, and mercuric

chlorides, magnesium, zinc, ferrous, manganese, cobalt, nickel, copper, and cadmium sulphates, lead and silver nitrates, and the gradual or immediate formation of precipitates or their failure to appear is recorded. The acids used are benzoic, phenylacetic, cinnamic,  $\beta$ -naphthoic, phthalic, naphthalic, *o*- and *p*-chlorobenzoic, 4-chlorophthalic, salicylic, 2- and 4-hydroxy-*m*-toluic, 3-hydroxy-*p*-toluic, 3- and 1-hydroxy- $\beta$ -naphthoic, 3 : 5-dihydroxybenzoic, *p*-hydroxybenzoic, *p*-methoxybenzoic, *o*-benzoylbenzoic, *o*-*p*-toluoylbenzoic, *o*-*m'*-nitro-*p'*-toluoylbenzoic, *o*- $\alpha$ -naphthoylbenzoic, *o*- and *p*-nitrobenzoic, 4-nitro-2-hydroxybenzoic, 5- and 4-chloro-2-nitrobenzoic, 2-nitro-6-hydroxybenzoic, 3-nitro-4-methoxybenzoic, 4-chloro-3 : 5-dinitrobenzoic, *o*-, *m*-, and *p*-aminobenzoic, 4-amino-2-hydroxybenzoic, and 3-amino-4-methoxybenzoic. The following sulphonic acids are employed: benzene-, 2 : 4- and 3 : 4-dimethylbenzene-,  $\alpha$ - and  $\beta$ -naphthalene-, 2 : 5- and 3 : 4-dichlorobenzenene-, 1-chloronaphthalene-, 5-dibromonaphthalene-2-, *p*-hydroxybenzenene-, 5- and 4-hydroxynaphthalene-1-, 6-hydroxynaphthalene-2-, 5- and 3-nitro-2-methylbenzene-, 4-chloro-3-nitrobenzene-, 3 : 4-dichloro-5-nitrobenzene-, 5-nitronaphthalene-1-, 6-nitronaphthalene-2-, 3 : 5-dinitro-4-methylbenzene-, 3 : 5-dinitro-2 : 4-dimethylbenzene-, and 2-chloro-3 : 5-dinitrobenzene-, sulphanilic, 4- and 3-sulphobenzoic, and 3-sulpho-4-hydroxybenzoic acids. Benzene-1 : 3-di-, naphthalene-2 : 5-, -2 : 7-, and -1 : 5-di-, 1-nitronaphthalene-3 : 6-di-, dibromonaphthalene-2 : 7-di-, 2 : 6-dinitrobenzene-1 : 4-di-, 1-carboxybenzene-2 : 4-di-, naphthalene-1 : 3 : 6-tri-, 1-chloronaphthalene-3 : 6 : 8-tri-, 2-chloronaphthalene-3 : 6 : 8-tri-, and 1-nitronaphthalene-3 : 5 : 7-tri-sulphonic acids are also used.

The barium, lead, and silver salts of the carboxylic acids are without exception sparingly soluble, as are those of copper, except in two cases in which the acids contain vicinal carboxyl groups. The precipitates are usually caseous or voluminous, whereas those of other salts are crystalline. This property appears to be constitutional and not simply attributable to the rapidity of the separation. In many cases, the separation of the precipitates occurs relatively very slowly, although the substances once formed are frequently very sparingly soluble. The phenomenon can scarcely be attributed to simple supersaturation, and it appears more likely that an equilibrium between true and complex or pseudo-salt exists in the solutions. In certain cases in which the initial salt form is sparingly soluble, this change is very obvious. Thus, for example, cadmium phenylacetate is immediately precipitated, but speedily re-dissolves and subsequently crystallises in a different form. Similar observations are recorded with the cadmium and copper salts of 4-hydroxy-*m*-toluic acid, the two varieties of the copper salt being further distinguished by their respective brown and green colours. Further confirmation of the existence of two distinct types of salts is found in the observation that the strontium salts in respect of solubility do not by any means always fall into line between the corresponding barium and calcium salts. Frequently the equilibrium between the two forms is only slowly established; this is well illustrated by the zinc,

manganese, and cobalt salts of naphthalic acid. The observation that separation is expedited by warming the solutions is regarded as strong evidence that a chemical reaction is here involved and that the phenomenon is not simply one of crystallisation.

The great solubility of the magnesium salts, which in many cases exceeds that of the sodium salts, is remarkable. The mercuric salts are generally freely soluble and are only precipitated when the parent acid forms a complete series of sparingly soluble salts or possibilities exist for the formation of internal complexes. The salts of zinc, manganese, ferrous iron, cobalt, nickel, and cadmium have medium solubilities; of these, the cadmium and to a less extent the zinc compounds tend to have the lowest solubilities and to approximate in their behaviour to the copper salts.

The influence of the organic residue on the solubility of the salts is discussed at considerable length. The observations, however, are of a preliminary nature.

The salts of the sulphonic acids are generally more freely soluble than those of the corresponding carboxylic acids. In this respect, the behaviour of naphthalene- $\beta$ -sulphonic acid is altogether exceptional, since its salts, in particular the magnesium compound, are distinguished by their sparing solubility (cf. A., 1921, 1, 508). The introduction of a nitro-group into the molecule appears to increase the solubility of the salts, but the effect is not further enhanced by the introduction of a second nitro-group. As in the case of the carboxylic compounds, the barium and lead salts are generally the most sparingly soluble, whereas the silver salts of the sulphonic acid are relatively soluble. The mercuric salts are, in general, freely soluble, whilst a great increase in solubility is noted in the case of the copper salts. The sodium salts in many cases do not dissolve freely.

The solubility of the salts derived from acids containing a sulphonic and a carboxyl group resembles in general that of the simple sulphonic acid. The introduction of a second sulphonic group into the molecule does not further increase the solubility of the salts.

H. W.

**Preparation of Phenylglycine-*o*-carboxylic Acid.** HERBERT L. HALLER (*J. Ind. Eng. Chem.*, 1922, 14, 1040—1044).—The reaction between anthranilic acid and chloroacetic acid for the preparation of phenylglycine-*o*-carboxylic acid was studied. The best yields were obtained under the following conditions: Concentration, 25 g. of anthranilic acid in 200 c.c. of water. Ratio, 2 mols. of anthranilic acid to 1 mol. of chloroacetic acid. Condensing agent, 2.33 mols. of sodium carbonate to 1 mol. of chloroacetic acid. Temperature, 90°. Time of reaction, 1 hour. The use of an alkali carbonate as a condensing agent gives a better yield than an equivalent amount of an alkali hydroxide.

H. C. R.

**Preparation of Allyl *p*-Aminobenzoate.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92300; from *Chem. Zentr.*, 1922, iv, 711; cf. Adams and Volweiler, A., 1921, i, 416).—

Compounds containing the *p*-nitrobenzoyl group are allylated and the allyl *p*-nitrobenzoate is reduced. For example, *p*-nitrobenzoyl chloride is heated with allyl alcohol at about 80°, or *p*-nitrobenzoic acid is esterified in the presence of hydrogen chloride. The allyl *p*-nitrobenzoate thus obtained is a light yellow oil crystallising on cooling, having m. p. 30° and b. p. 146–152°/3 mm. Allyl *p*-aminobenzoate obtained by reduction of the latter compound forms almost colourless needles, m. p. 54°. It is a local anæsthetic.

G. W. R.

**Preparation of Complex Silver Compounds.** F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 1356912, Swiss Pat. 90809, 91108, and 91109; from *Chem. Zentr.*, 1922, iv, 711; cf. Myers, A., 1921, i, 843).—Organic or inorganic silver salts are allowed to react with thio-acyl derivatives of aromatic amines. *α*-Thiolacetylamidophenol, an amorphous, yellow powder, m. p. 105°, from chloroacetylamidophenol and sodium persulphide, is allowed to react with silver nitrate solution. The silver *α*-thiolacetylamidophenol obtained contains 37.2% of silver and gives no precipitate with sodium chloride, hydrogen sulphide, or ammonium sulphide solutions. From sodium *α*-thiolacetylamidosalicylate, silver sodium *α*-thiolacetylamidosalicylate is obtained. *α*-Thiolacetylamidosalicylic acid, obtained from chloroacetylamidosalicylic acid and sodium persulphide, is a light yellow powder, m. p. 223°. It gives a sodium salt. Similar products are obtained by the action of silver nitrate on the sodium salts of thiolisovalerylamidosalicylic acid and thiolpropionylamidosalicylic acid, respectively. The latter compound has m. p. 226°. These acids are prepared by the action of sodium persulphide on bromoisovalerylamidosalicylic acid and bromopropionylamidosalicylic acid, respectively.

G. W. R.

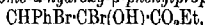
**The Resolution of Phenoxypropionic Acid and *o*-Nitrophenoxypropionic Acid into their Active Components.** E. FOURNEAU and G. SANDULESCO (*Bull. Soc. chim.*, 1922, [iv], 31, 888–893).—In resolving acids into their optical isomerides, the choice of yohimbine as a base leads to the formation of salts which crystallise readily and are separable without difficulty. Details are given of the separation of the phenoxypropionic acids as salts of yohimbine and of the *o*-nitrophenoxypropionic acids as salts of yohimbine and of cinchonine. In both cases the active form of the acids melt at a lower temperature than the racemic mixtures; *d*- and *l*-phenoxypropionic acids have m. p. 87°, the mixture 115°; the corresponding temperatures for *o*-nitrophenoxypropionic acid being 111–112° and 157°.

H. J. E.

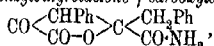
**Ethyl Phenylpyruvate.** II. H. GAULT and R. WEICK (*Bull. Soc. chim.*, 1922, [iv], 31, 993–1026; cf. A., 1922, i, 1024).—Various reactions of the three isomeric forms of ethyl phenylpyruvate were studied and grouped according to whether they were (a) different in the case of the enolic and ketonic forms, or (b) common to all three forms. Among the former are the color-

ation obtained in presence of ferric chloride, the formation of additive bromine derivatives, the addition of phenylcarbimide yielding the phenylurethane, and the action of hydrochloric acid, which reactions the authors regard as fundamental for distinguishing between the  $\alpha$ - and  $\beta$ - and the  $\gamma$ -forms. The reactions common to all three isomerides include formation of esters, lactonisation, and condensation. An attempt to investigate the isomerism of ring-substituted derivatives of ethyl phenylpyruvate was abandoned owing to the difficulty of preparing these substances. The refractive indices of the isomerides were found to be;  $\beta$ ,  $n_D^{20}$  1.49735,  $\gamma$ ,  $n_D^{20}$  1.49821; the value for the  $\alpha$ -ester was not determined by reason of the rapid oxidation of the substance in air. Theoretical consideration of the results indicates that the  $\beta$ -form is enolic, and on chemical grounds the  $\alpha$ -ester is considered to be similar, the two being stereoisomerides; it is not possible, as yet, to decide which is the *cis* and which the *trans* form. The  $\gamma$ -ester has, on theoretical grounds, the ketonic form.

The following substances do not appear to have been previously described: *Ethyl  $\beta$ -bromophenylpyruvate*,  $\text{CHPhBr}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , a mobile, yellow liquid of characteristic odour, b. p. 182—184.5°/20 mm.; *Ethyl  $\alpha\beta$ -dibromo- $\alpha$ -hydroxy- $\beta$ -phenylpropionate*,



a yellow, crystalline solid, m. p. not determined, as the substance is too unstable: it is stated that this is the first instance of the isolation of a brominated enolic compound; *Ethyl  $\alpha$ -acetoxy- $\beta$ -phenylpropionate*, a colourless oil of pleasant odour, b. p. 161—163°/15 mm.; *Ethyl  $\alpha$ -benzyloxy- $\beta$ -phenylpropionate*, yellow oil, b. p. 225—226°/15 mm.; *Ethyl  $\alpha$ -acetoxy-*cinnamate**, white crystals, m. p. 33.5°; *Ethyl  $\alpha$ -benzyloxy-*cinnamate**, white needles, m. p. 87°;  *$\alpha$ -Keto- $\beta$ -phenyl- $\gamma$ -benzylbutyrolactone- $\gamma$ -carboxylamide*,



white crystals, m. p. 229°; *2-benzylidene-1:4-dihydroquinazalone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{NH}\cdot\text{C}\cdot\text{CHPh} \\ \diagdown \text{NH}\cdot\text{CO} \end{array}$ , yellowish-white crystals, m. p. 210°.

H. J. E.

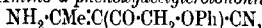
**Preparation of an  $\alpha\beta$ -Tetrahydronaphtholcarboxylic Acid and its Ester and Acyl Derivative.** TETRALIN G. M. B. H. (D.R.-P. 357663; from *Chem. Zentr.*, 1922, iv, 761).—An anhydrous alkali salt of  $\alpha\beta$ -tetrahydronaphthol is treated with carbon dioxide at temperatures above 100°. After acidification, the resulting product is changed into esters or acyl derivatives by the usual methods. The potassium salt of  $\alpha\beta$ -tetrahydronaphthol, freed from water in a stream of hydrogen at 150—160°, is treated with carbon dioxide under pressure for several hours at 160—170°. After one molecule of carbon dioxide has been absorbed, the product is dissolved in water and acidified with hydrochloric acid. The  $\beta$ -tetrahydronaphthol- $\alpha$ -carboxylic acid thus obtained forms colourless needles, m. p. 177—178°. It gives a deep blue coloration with ferric chloride. The methyl ester has b. p. 184—185°/20 mm.; it

has an odour like that of ethyl acetoacetate, and forms a crystalline mass on keeping. By the action of acetic anhydride on the carboxylic acid at  $100^{\circ}$  in the presence of sulphuric acid,  $\beta$ -acetoxytetrahydronaphthalene-o-carboxylic acid, m. p.  $142-143^{\circ}$ , is obtained.

G. W. R.

**Certain Acidic Derivatives of "Dinitriles" and  $\beta$ -Aminocrotonic Esters.** ERICH BENARY and MARTIN ROSENFELD (*Ber.*, 1922, 55, [B], 3417-3429; cf. Benary and Schmidt, A., 1921, i, 776).—In continuation of previous work, the introduction of the phenoxyacetyl group into imidoacetonitrile, imidobenzoylacetonitrile, and imidotoluoylacetonitrile has been investigated. The use of the ester in the presence of sodium ethoxide leads to the production of a *N*-derivative, whereas *C*-compounds are produced from the acid chloride in the presence of pyridine. The condensation of the ester with these substances in the presence of potassium ethoxide has been described by Meyer (A., 1914, i, 996), but evidence is now adduced to show that his conception of the products as *C*-derivatives is incorrect.

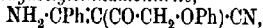
Whereas in the previous instances investigated the production of uniform *C*- or *N*-derivatives has been observed according to the mode of procedure, it is found that cinnamoyl chloride and diacetonitrile give a mixture of about equal quantities of the two isomerides, whereas cinnamic ester and sodium ethoxide give only the *N*-derivative.  $\beta$ -Amino- $\alpha$ -phenoxyacetylcrotononitrile,



slender, colourless needles, m. p.  $167^{\circ}$ , is prepared by the action of phenoxyacetyl chloride on imidoacetylacetonitrile in anhydrous ethereal solution in the presence of pyridine. It is converted by *N*-sodium hydroxide solution into  $\beta$ -hydroxy- $\alpha$ -phenoxyacetylcrotononitrile,  $\text{OH}\cdot\text{CMe:C(CO}\cdot\text{CH}_2\cdot\text{OPh)}\cdot\text{CN}$ , almost colourless needles, m. p.  $138^{\circ}$ , the enolic nature of which is established by the isolation of the green copper salt.  $\beta$ -Amino- $\alpha$ -phenoxyacetylcrotononitrile is converted by phenylhydrazine into 4-cyano-1-phenyl-5-phenoxyethyl-3-methylpyrazole,  $\text{CMe}\cdot\text{C}\begin{smallmatrix} \text{C(CN)} \\ \text{N}\cdot\text{NPh} \end{smallmatrix}\cdot\text{C}\cdot\text{CH}_2\cdot\text{OPh}$ , colourless needles, m. p.

$73-74^{\circ}$ , which is also prepared by the action of phenylhydrazine on  $\beta$ -hydroxy- $\alpha$ -phenoxyacetylcrotononitrile in acetic acid solution. *N*- $\beta$ -Phenoxyacetylamidocrotononitrile,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CN}$ , m. p. ( $\alpha$ -form)  $96^{\circ}$ , ( $\beta$ -form)  $123^{\circ}$  (cf. Meyer, *loc. cit.*), is decomposed by *N*-sodium hydroxide solution with the formation of phenoxyacetic acid, and by phenylhydrazine in acetic acid solution with production of phenoxyacetic acid phenylhydrazide.

$\beta$ -Amino- $\alpha$ -phenoxyacetylcinnamonitrile,



glassy, hexagonal plates, m. p.  $152^{\circ}$ , is prepared from imidobenzoylacetonitrile, pyridine, and phenoxyacetyl chloride in the presence of ether, and is transformed into  $\beta$ -hydroxy- $\alpha$ -phenoxyacetylcinnamonitrile,  $\text{OH}\cdot\text{CPh:C(CO}\cdot\text{CH}_2\cdot\text{OPh)}\cdot\text{CN}$ , lustrous leaflets, m. p.  $118^{\circ}$ . With phenylhydrazine in acetic acid solution (50%), it gives 4-cyano-1:3-diphenyl-5-phenoxyethylpyrazole, slender, colourless

needles, m. p. 158°.  $\beta$ -Phenoxyacetylamidocinnamionitrile,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$ , m. p. ( $\alpha$ -form) 95° (Meyer, *loc. cit.*, gives 87°), m. p. ( $\beta$ -form) 114°, is converted by *N*-sodium hydroxide solution into phenoxyacetic acid, and by phenylhydrazine into phenoxyacetic hydrazide. The product obtained by coupling the  $\beta$ -variety with diazobenzene chloride in alcoholic solution has m. p. 140° (Meyer, *loc. cit.*, gives 110°), and appears to have the composition  $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_4$ ; its nitrogen content is greater than that found by Meyer.

$\beta$ -Amino- $\alpha$ -phenoxyacetyl- $\beta$ -*p*-tolylacrylonitrile,  
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CO}\cdot\text{CH}_2\cdot\text{OPh})\cdot\text{CN}$ ,

large, colourless needles, m. p. 178°,  $\beta$ -hydroxy- $\alpha$ -phenoxyacetyl- $\beta$ -*p*-tolylacrylonitrile,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{CO}\cdot\text{CH}_2\cdot\text{OPh})\cdot\text{CN}$ , colourless crystals, m. p. 141°, and 4-cyano-1-phenyl-3-*p*-tolyl-5-phenoxy-methylpyrazole, long needles, m. p. 167°, are obtained by similar methods.  $\beta$ -Phenoxyacetyl-amido- $\beta$ -*p*-tolylacrylonitrile, m. p. 148° (cf. Meyer, *loc. cit.*), is decomposed by sodium hydroxide or phenylhydrazine in the manner described for the analogous *N*-compounds.

Ethyl chloroformate, imidoacetylacetonitrile, and pyridine give an unstable substance,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_3$ , a pale yellow, crystalline powder, m. p. 129–130° (decomp.). It is decomposed by boiling sodium hydroxide solution with the evolution of ammonia and pyridine. When preserved in the presence of water or alcohol, it forms a yellowish-red powder, decomp. 265–280°.

Imidoacetylacetonitrile, cinnamoyl chloride, and pyridine in the presence of ether yield a mixture of  $\beta$ -amino- $\alpha$ -cinnamoylcrotononitrile,  $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$ , colourless needles, m. p. 198–199°, and  $\beta$ -cinnamoylaminocrotononitrile,

$\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CN}$ ,

colourless, quadratic plates, m. p. 191–192°. The latter substance is transformed by *N*-sodium hydroxide solution into ammonia and cinnamic acid, and by bromine in the presence of chloroform into  $\beta$ - $\alpha'$ -bromocinnamoylaminocrotononitrile,

$\text{CHPh}\cdot\text{CBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CN}$ ,

a colourless, crystalline powder, m. p. 144–145°.  $\beta$ -Amino- $\alpha$ -cinnamoylcrotononitrile is converted by sodium hydroxide solution into  $\beta$ -hydroxy- $\alpha$ -cinnamoylacetone,  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$  (enolic form), sulphur-yellow needles, m. p. 130°, and by phenylhydrazine into 4-cyano-1-phenyl-5-styryl-3-methylpyrazole, slender, colourless needles, m. p. 134°.  $\beta$ -Amino- $\alpha$ -cinnamoylcrotononitrile dibromide,  $\text{CH}_3\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{Ph}$ , crystallises in slender needles, m. p. 220° (decomp.) after darkening at 205°.

$\beta$ -Amino- $\alpha$ -cinnamoylcinnamionitrile,

$\text{NH}_2\cdot\text{CPh}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$ ,

long, colourless needles, m. p. 173° (prepared from imidobenzoylacetoneitrile, cinnamoyl chloride, and pyridine) is converted in the usual manner into  $\beta$ -hydroxy- $\alpha$ -cinnamoylcinnamionitrile,

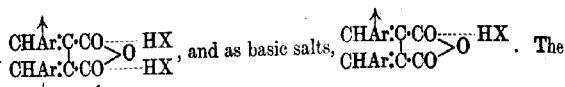
$\text{OH}\cdot\text{CPh}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$ ,

lemon-yellow needles, m. p. 140°, and 4-cyano-1:3-di-phenyl-5-styrylpyrazole, colourless needles, m. p. 205° (decomp.).  $\beta$ -Cinnamoylaminocinnamionitrile,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$ , prepared

from the nitrile, cinnamic ester, and potassium ethoxide, crystallises in long, colourless needles or leaflets, m. p. 134—135°.

*Ethyl β-amino-α-phenoxyacetylcrotonate*,  
 $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{CH}_2\cdot\text{OPh})\cdot\text{CO}_2\text{Et}$ ,  
 m. p. 159°, is prepared by the action of ethyl β-aminocrotonate or phenoxyacetyl chloride and pyridine in the presence of ether. It is converted by the successive action of phenylhydrazine and alcoholic potassium hydroxide solution into 1-phenyl-3-phenoxy-methyl-5-methylpyrazole-4-carboxylic acid,  $\text{N}\begin{smallmatrix} \text{C}(\text{CH}_2\cdot\text{OPh}) \\ \text{NPh}-\text{CMe} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{H}$ , brown needles, m. p. 178°. *Ethyl β-phenoxyacetylaminocrotonate*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , prepared by the ester method, crystallises in colourless needles, m. p. 88°. H. W.

**Halochromism of the Fulgides.** HANS STOBBE and RICHARD DIETZEL (*Ber.*, 1922, 55, [B], 3567—3580).—The absorption spectra of diphenylfulgide,  $\text{CHPh}\cdot\text{C}\cdot\text{CO}>\text{O}$ , and the corresponding tri- and tetra-phenyl compounds have been investigated. The substances dissolve in indifferent media such as light petroleum, alcohol, and chloroform, yielding solutions of their own colour in the solid state, whereas in strongly acidic liquids such as mono-, di-, and tri-chloroacetic acids they give solutions of a much darker colour. The isolation of the fulgides from these solutions in the form of their solid molecular compounds has not been accomplished, since they dissociate into their components in the presence of water, even when a large excess of acid is used. The investigation has therefore been confined to their solutions in chloroform and the three chloroacetic acids. The absorption of light is dependent on the strength of the acid; in the weakest of these, the limit of absorption approximates to that observed in chloroform solution. It therefore appears that, even in the presence of an excess of the acid, the fulgide is present partly as the monochloroacetate and partly as fulgide, and that this equilibrium is most markedly displaced in favour of the salt in the trichloroacetic acid solution. The constitution of the fulgide has a regular effect on the absorption of light. The ultra-violet spectra have also been examined. The absorption of solutions of the fulgides in chloroform are characterised by an ultra-violet band in the region of short wave-length and a "colour band" in the visible region. Increase in the number of the phenyl groups has no effect on the former, but causes an increased intensity in the latter and also a considerable displacement towards the red end. In the three chloroacetic acid solutions, the absorption is similar, but differs from that observed in chloroform. In place of the two bands of the latter, the ultra-violet band in the chloroacetic acid solutions disappears and is replaced by a narrow colour band which is very strongly displaced towards the red end. This displacement of the band is characteristic of the transition from a saturated to an unsaturated compound. It appears, therefore, that (in accordance with Pfeiffer's method of formulation) the fulgides function as normal salts,



formulae, however, are to be regarded only as structural approximations, since they do not take into account the established influence of the number of aryl radicles on the strength of the halochromism.

The colour of the arylfulgides is attributable to the ortho-quinonoid tetrahydrofuran nucleus,  $\begin{array}{c} >\text{C}:\text{C}=\text{CO} \\ >\text{C}:\text{C}=\text{CO} \end{array} >\text{O}$ , and to the

number and nature of the aryl substituents. The effect of the opening of the ring or alteration of its unsaturated character has been examined in the cases of diphenylfulgenic acid,  $\text{CO}_2\text{H}:\text{C}(\text{CHPh})\text{C}(\text{CHPh})\text{CO}_2\text{H}$ , triphenylfulgenic acid, and tetrahydrodiphenylfulgide (dibenzylsuccinic anhydride). The absorption curves of the fulgenic acids in chloroform are precisely similar to those in the chloroacetic acids, so that their molecular condition in the solutions must be almost the same. The halochromism which is so strongly marked with the fulgides has practically disappeared after the opening of the ring and loss of the quinonoid nucleus. A comparison of the absorption curve of tetrahydrodiphenylfulgide with that of diphenylfulgide shows that the former is much more transparent, and also that the narrow ultra-violet band of the latter persists after hydrogenation. On the other hand, the absorption curves of tetrahydrodiphenylfulgide in alcohol and trichloroacetic acid are very similar. In this case, as with the fulgenic acids, halochromism is scarcely perceptible; the carbonyl groups are not in themselves capable of uniting with chloroacetic acid. For this purpose, the ethylenic linkings of the non-hydrogenated fulgide are indispensable; they strengthen the unsaturated nature of the carbon atom, and thus indirectly cause a deepening of the colour.

H. W.

**Resorcinolphenylsuccinein.** ARTHUR LAPWORTH and JOHN ALEXANDER McRAE (T., 1922, 121, 2722—2724.)

**A Condensation of Dehydrodeoxycholic Acid.** TOMIHIDE SHIMIZU (Z. physiol. Chem., 1922, 123, 159—163).—Dehydrodeoxycholic acid on treatment with hydrogen chloride in alcoholic solution not only is esterified, but also an aldol condensation takes place between a keto-group of one molecule and a methylene group of another, and in addition the hydroxyl group formed in this process is replaced by chlorine, a compound,  $\text{C}_{32}\text{H}_{70}\text{O}_7\text{Cl}$ , m. p.  $204^\circ$ , being formed. On treatment with sodium ethoxide, this compound is hydrolysed and also loses hydrogen chloride, to yield an unsaturated dibasic acid,  $\text{C}_{48}\text{H}_{70}\text{O}_7$ , six-sided prisms, m. p.  $276^\circ$ . In addition to the above-mentioned condensation product, the simple ethyl ester, lustrous leaflets, m. p.  $108^\circ$ , can also be isolated, and if methyl alcohol is used instead of ethyl alcohol, no condensation takes place, the sole product being methyl dehydrodeoxycholate, fine needles aggregating into leaflets, m. p.  $130^\circ$ .

W. O. K.

**The Bile Acids. XV.  $\psi$ -Choloidanic Acid.** HEINRICH WIELAND (*Z. physiol. Chem.*, 1922, **123**, 237—245).— $\psi$ -Choloidanic acid formed, along with choloidanic acid, in the oxidation of deoxybilanic acid has the formula  $C_{24}H_{34}O_{10}$ . It forms a neutral tetramethyl ester,  $C_{28}H_{42}O_{10}$ , a dimethyl ester,  $C_{26}H_{38}O_{10}$ , long needles, m. p. 268°, and a barium salt,  $C_{28}H_{36}O_{10}Ba$ , glistening needles. When heated, it loses carbon dioxide and water, to form *pyro- $\psi$ -choloidanic acid*,  $C_{22}H_{30}O_6$ , lustrous leaflets, m. p. 246° (hydrate,  $C_{22}H_{30}O_6 \cdot H_2O$ , glistening needles, m. p. 115—116°). The dimethyl ester of  $\psi$ -choloidanic acid yields, when heated, the neutral ester of a monobasic acid,  $C_{23}H_{29}O_5 \cdot OMe$ , m. p. 192°. W. O. K.

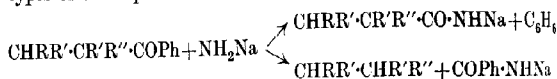
**The Bile Acids. XIV. Cilianic Acid, Ciloidanic Acid, and Biloidanic Acid.** HEINRICH WIELAND and ORTO SCHLICH-TUNG (*Z. physiol. Chem.*, 1922, **132**, 213—236; cf. A., 1922, i, 838).—Ciloidanic acid,  $C_{29}H_{34}O_{13}$ , may be oxidised by nitric acid, *d* 1.52, to biloidanic acid,  $C_{22}H_{32}O_{12}$ . The formula given previously for this acid,  $C_{23}H_{34}O_{12}$ , is not correct, and it is found that it is identical with norsolanellanic acid. When heated with sulphuric acid, ciloidanic acid loses carbon dioxide and carbon monoxide, to yield a *keto-tetracarboxylic acid*,  $C_{22}H_{32}O_9$ , needles, m. p. 238°,  $[\alpha]_D^{25} + 73.5^\circ$ . This keto-carboxylic acid on oxidation by nitric acid (*d* 1.4) yields biloidanic acid in a very pure form, and by this means the new formula has been established. Biloidanic acid when heated in a vacuum loses water and carbon dioxide to yield *pyrobiloidanic acid*,  $C_{21}H_{28}O_9$ , fine, microscopic prisms, m. p. 193—195°. If this acid is heated with alkali, an internal lactone ring is hydrolysed, and an acid,  $C_{21}H_{30}O_9 \cdot H_2O$ , is formed. The constitution of the bile acids is discussed in the light of these results, and modifications of the earlier formulæ are suggested. W. O. K.

**The Acidity of Gallaldehyde.** M. NIERENSTEIN (*Ber.*, 1922, **55**, [B], 3581).—The presumed great acidity of gallaldehyde has been regarded by Rosenmund and Zetzsche (A., 1918, i, 301) as indirect evidence against Nierenstein's observation (A., 1909, i, 402) that gallaldehyde is formed by the hydrolysis of gallotannin. The recognition that the aldehyde is not so acidic as was supposed (Rosenmund and Pfannbuch, A., 1922, i, 1030) invalidates this argument. H. W.

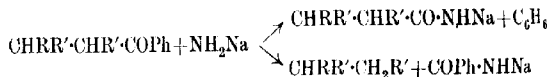
**The Condensation of *o*-Halogenoketones with Aldehydes.** SVEN BODFORSS (*Ber.*, 1922, **55**, [B], 3581).—A claim for priority against Bauer and Werner (A., 1922, i, 1034; cf. Bodfors, A., 1917, i, 223; 1919, i, 211). H. W.

**Some  $\alpha\alpha\beta\beta$ -Tetra-substituted Propiophenones and the Products they yield on Decomposition with Sodamide.** GEORGES ALBESCO (*Ann. Chim.*, 1922, **18**, 216—262; cf. Haller and Bauer, A., 1909, i, 108, 654; 1910, i, 300; Dumesnil, A., 1911, i, 718).—A study of the action of organo-magnesium compounds on phenyl styryl ketone and phenyl methylphenedioxystyryl ketone with formation of  $\beta\beta$ -substituted acetophenones and subsequent substitution

in the  $\alpha$ -position with methyl or ethyl groups, resulted in the preparation of the following compounds. *Phenyl  $\alpha$ -ethylstyryl ketone*, a viscous liquid, b. p.  $208^{\circ}/14$  mm.  *$\beta$ -Phenyl- $\beta$ -p-tolyl-propiophenone*, colourless crystals, m. p.  $96^{\circ}$ , b. p.  $254^{\circ}/12-13$  mm.  *$\beta$ -Methylenedioxyphenyl- $\beta$ -methylpropiophenone*, prisms, m. p.  $73^{\circ}$ .  *$\beta$ -Methylenedioxyphenyl- $\beta$ -ethylpropiophenone*, colourless prisms, m. p.  $58^{\circ}$ , b. p.  $233^{\circ}/11$  mm.  *$\beta$ -Phenyl- $\beta$ -methylenedioxyphenylpropiophenone*, crystals, m. p.  $97^{\circ}$ , b. p.  $280^{\circ}/14$  mm.  *$\beta\beta$ -Diphenyl- $\alpha\alpha$ -dimethylpropiophenone*, m. p.  $90^{\circ}$ .  *$\beta\beta$ -Diphenyl- $\alpha$ -ethylpropiophenone*, m. p.  $118^{\circ}$ .  *$\beta$ -Phenyl- $\alpha$ -methyl- $\beta$ -ethylpropiophenone*, crystals, m. p.  $54-55^{\circ}$ .  *$\beta$ -Phenyl- $\alpha\alpha$ -dimethyl- $\beta$ -ethylpropiophenone*, mobile liquid, b. p.  $195^{\circ}$ ;  *$\beta$ -phenyl- $\alpha\alpha$ -triethylpropiophenone*, mobile liquid, b. p.  $195^{\circ}$ , 760 mm.;  *$\beta$ -phenyl- $\beta$ -p-tolyl- $\alpha$ -methylpropiophenone*, colourless crystals, m. p.  $116^{\circ}$ ;  *$\beta$ -phenyl- $\beta$ -p-tolyl- $\alpha$ -ethylpropiophenone*, colourless crystals, m. p.  $131^{\circ}$ , b. p.  $252^{\circ}/12$  mm.  *$\beta$ -Phenyl- $\beta$ -methoxyphenyl- $\alpha$ -methylpropiophenone*, m. p.  $128^{\circ}$ .  *$\beta$ -Methylenedioxyphenyl- $\alpha\beta$ -dimethylpropiophenone*, m. p.  $70^{\circ}$ .  *$\beta$ -Methylenedioxyphenyl- $\alpha\alpha\beta$ -trimethylpropiophenone*, colourless, mobile liquid, b. p.  $230^{\circ}$ .  *$\beta$ -Methylenedioxyphenyl- $\alpha$ -methyl- $\beta$ -ethylpropiophenone*, an oil, b. p.  $236^{\circ}/15$  mm.  *$\beta$ -Methylenedioxyphenyl- $\alpha\alpha$ -dimethyl- $\beta$ -ethylpropiophenone*, an oil, b. p.  $235^{\circ}/11$  mm.;  *$\beta$ -methylenedioxyphenyl- $\alpha\beta$ -diethylpropiophenone*, an oil, b. p.  $234-235^{\circ}/13-14$  mm.  *$\beta$ -Phenyl- $\beta$ -methylenedioxyphenyl- $\alpha$ -methylpropiophenone*, needles, m. p.  $128^{\circ}$ . In those cases in which both  $\beta$ -substituents are of aromatic type, the second  $\alpha$ -substitution takes place with difficulty. The action of sodamide on the tetra-substituted derivatives results in fission of the ketone molecule at two different points, the two types of decomposition occurring to the same extent:



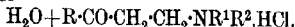
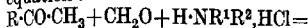
The reaction affords a ready means of preparing tetra-substituted propionic acids. The action of sodamide under the influence of heat on the ketones which are mono-substituted in the  $\alpha$ -position results in formation of two products:



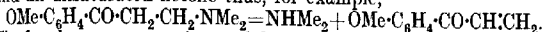
Among the substances obtained by the action of sodamide are the following.  *$\beta\beta$ -Diphenyl- $\alpha\alpha$ -dimethylpropionamide*, white crystals, m. p.  $120^{\circ}$ .  *$\alpha\alpha$ -Diphenyl- $\beta$ -methylpropane*, mobile, colourless liquid, b. p.  $145^{\circ}/13$  mm.  *$\gamma$ -Phenyl- $\beta$ -methylpentane*, mobile, colourless liquid, b. p.  $200^{\circ}$ .  *$\beta$ -Phenyl- $\alpha\alpha$ -dimethylvaleramide*, viscous liquid, b. p.  $180^{\circ}/11$  mm.  *$\delta$ -Phenyl- $\gamma$ -ethylhexane*, mobile, colourless liquid, b. p.  $205^{\circ}$ .  *$\beta$ -Phenyl- $\alpha\alpha$ -dimethylvaleric acid*, crystals, m. p.  $82^{\circ}$ .  *$\beta$ -Phenyl- $\alpha\alpha$ -diethylvaleric acid*, m. p.  $68-69^{\circ}$ .  *$\beta\beta$ -Diphenyl- $\alpha$ -ethylpropionamide* [ *$\alpha$ -benzhydrylbutyramide*], colourless crystals, m. p.  $151^{\circ}$ .

H. J. E.

**The Synthesis of  $\beta$ -Keto-bases from Fatty-aromatic Ketones, Formaldehyde, and Secondary Amines.** C. MANNICH and D. LAMMERING (*Ber.*, 1922, 55, [B], 3510—3526).— $\beta$ -Ketonic bases may be prepared from the salts of secondary amines, formaldehyde, and fatty-aromatic ketones in accordance with the equation:



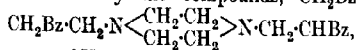
Reaction is usually effected by boiling molar quantities of the salt and concentrated formaldehyde solution with the fatty-aromatic ketone. Frequently, it is advantageous to work in the absence of moisture, for example, by heating the amine salt and ketone with paraformaldehyde in the presence of alcohol, in which case an excess of aldehyde must be used. The synthesis is capable of considerable variation. The ketonic component may be acetophenone, methoxyacetophenone, acetoveratrone, propiophenone, deoxybenzoin, or  $\beta$ -acetyltetrahydronaphthalene, but apparently not *p*-acetylamidoacetophenone, whereas the basic component may be dimethylamine, diethylamine, piperidine, tetrahydroisoquinoline, or piperazine, but not tetrahydroquinoline. The keto-bases and their hydrochlorides are, in general, fairly stable, but are more or less rapidly decomposed at their boiling points into a tertiary amine and an unsaturated ketone thus, for example,



The free bases are sometimes solid, and are then purifiable by crystallisation, and sometimes liquid; in the latter case, they cannot be purified, since they decompose on distillation under diminished pressure. In many cases, they have been further characterised by the formation of oximes, but the process does not occur smoothly when the dimethylamino-group is present in the molecule. The  $\beta$ -keto-bases are most conveniently reduced to the corresponding secondary alcohols by hydrogen in the presence of palladium, but zinc dust and hydriodic acid may also be used. Sodium and alcohol are unsuitable, since loss of the amine residue is caused thereby; aluminium amalgam in the presence of moist ether reduces the ketones to pinacone-like substances. The alcoholic bases, in contrast to the ketonic compounds, are quite stable, and can be distilled under diminished pressure without decomposition.

The synthesis just described allows the ready preparation of substances which contain nitrogen in the  $\gamma$ -position to the benzene nucleus. In contrast to the behaviour of the similar substances containing the nitrogen in the  $\beta$ -position, the compounds,

$OH \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2$ , and  $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2$ , do not cause any rise in the blood pressure. Anaesthetising properties are shown by the compounds,  $CH_2Bz \cdot CH_2 \cdot C_5NH_{10}$ .



$CH_2Bz \cdot CH_2 \cdot N < \begin{array}{c} CH_2 \\ CH_2 \cdot CH_2 \end{array} > C_6H_4$ , and  $CHPhBz \cdot CH_2 \cdot C_5NH_{10}$  (all of which contain the benzoyl group, but not in the form of ester), and by the substances  $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$ .

$C_{10}H_{11}\cdot CO\cdot CH_2\cdot CH_2\cdot NMe_2$ ,  $C_{10}H_{11}\cdot CO\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$ , and  $OMe\cdot C_6H_4\cdot CO\cdot CHMe\cdot CH_2\cdot C_5NH_{10}$ . The  $\beta$ -amino-alcohols are not anaesthetics in themselves, but exhibit extremely active properties in the form of their benzoates, being in some cases markedly more potent than cocaine. Unfortunately, they have also an irritant action.

The following individual substances are described.  $\beta$ -Piperidinoethyl phenyl ketone,  $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot C_6H_5$ , a colourless, odourless liquid (hydrochloride, m. p. 192–193°, picrate, needles, m. p. 180.5°, and oxime, needles, m. p. 143°). 1:6-Dipiperidino-3:4-diphenylhexane-3:4-diol,

$C_5NH_{10}\cdot CH_2\cdot CH_2\cdot C_6H_4(OH)\cdot C_6H_4(OH)\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$ , ( $\alpha$ -form), m. p. 238° (decomp.) [hydrochloride, decomp. about 270°], ( $\beta$ -form), large plates, m. p. 115°.  $\beta$ -Piperidinoethylphenylcarbinol,  $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$ , leaflets, m. p. 68–69° (hydrochloride, m. p. 138°; picrate, needles, m. p. 103°; benzoate, flattened needles, m. p. 170°; p-nitrobenzoate, brown needles, m. p. 104°; p-aminobenzoate, m. p. 118°).  $\beta$ -Tetrahydroisoquinolinoethyl phenyl ketone,  $C_6H_4\cdot CH_2\cdot CH_2\cdot N\langle\begin{smallmatrix} CH_2 \\ CH_2\cdot CH_2 \end{smallmatrix}\rangle\cdot C_6H_5$ , a viscous liquid

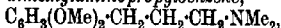
which solidifies in a freezing mixture, and its hydrochloride, m. p. 188°. 1:4-Di- $\beta$ -benzoyl ethylpiperazine, crystalline granules, m. p. 141° (hydrochloride, decomp. 190°; picrate, needles, decomp. above 190°; diaxime, m. p. 245°). p-Methoxyphenyl  $\beta$ -dimethylaminoethyl ketone hydrochloride,  $C_6H_4(OMe)\cdot CO\cdot CH_2\cdot CH_2\cdot NMe_2\cdot HCl$ , needles, m. p. 181° (corresponding picrate, m. p. 145°); the hydrochloride is decomposed at 180°/20 mm., into dimethylamine hydrochloride and p-anisyl vinyl ketone, b. p. 138–142°/20 mm., m. p. 19° (corresponding dibromide, prisms, m. p. 71°). ? 1-Phenyl-3-p-anisylpyrazoline,

$\begin{smallmatrix} NPh \\ | \\ CH_2\cdot CH_2 \end{smallmatrix} \rangle C\cdot C_6H_4\cdot OMe$ , m. p. 105° (from the vinyl ketone and phenylhydrazine). Anisyl ethyl ketone semicarbazone, m. p. 176°. p-Hydroxyphenyl  $\beta$ -dimethylaminoethyl ketone hydriodide, pale yellow leaflets, m. p. 205° (from the methoxy compound and hydriodic acid), and the corresponding hydrochloride, pale yellow leaflets, m. p. 189°. p-Anisyl- $\beta$ -dimethylaminoethylcarbinol, b. p. 146–148°/30 mm., m. p. 53° (hydrochloride, needles, m. p. 203–204°; hydrochloride of the corresponding benzoate, m. p. 174°).  $\beta$ -Piperidinoethyl p-anisyl ketone, a liquid which solidifies in a freezing mixture (hydrochloride, needles, m. p. 216°; picrate, short needles, m. p. 165°; oxime, needles, m. p. 136°). 1:4-Di-p-anisylethylpiperazine,  $C_4N_2H_8(CH_2\cdot CH_2\cdot CO\cdot C_6H_4\cdot OMe)_2$ , pale yellow leaflets, m. p. 173° after darkening at 171° (the hydrochloride darkens without melting above 150°).  $\beta$ -Piperidinoisopropyl p-anisyl ketone,  $OMe\cdot C_6H_4\cdot CO\cdot CHMe\cdot CH_2\cdot C_5NH_{10}$ , a liquid prepared from piperidine, p-anisyl ethyl ketone, and paraformaldehyde (hydrochloride, leaflets, m. p. 178°; oxime, m. p. 94°). 3:4-Dimethoxyphenyl- $\beta$ -dimethylaminoethyl ketone,

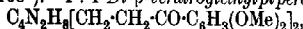
$C_6H_3(OMe)_2\cdot CO\cdot CH_2\cdot CH_2\cdot NMe_2$ , a viscous liquid (hydrochloride, needles, m. p. 181–182°; picrate, needles, m. p. 157°). 3:4-Dihydroxyphenyl  $\beta$ -dimethylaminoethyl ketone (from the hydrochloride of the corresponding methoxy-

compound and hydriodic acid), isolated as the *hydriodide*, pale yellow crystals, m. p. 196°, and *hydrochloride*, needles, m. p. 179°.

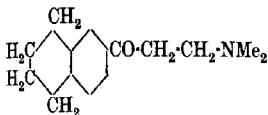
3:4-Dimethoxy-γ-dimethylaminopropylbenzene,



a colourless liquid, b. p. 161–164°/30 mm., prepared unexpectedly by the reduction of the corresponding ketone by hydrogen in the presence of palladised animal charcoal (*hydrochloride*, needles, m. p. 195°). β-Piperidinoethyl-3:4-dimethoxyphenyl ketone, m. p. 113° (*hydrochloride*, small prisms, m. p. 183°; *picrate*, m. p. 180°; *oxime*, needles, m. p. 168°). 1:4-Di-β-veratroylethylpiperazine,



yellow needles, m. p. 168° (*hydrochloride*, short needles which decompose without melting above 150°). Veratryl β-diethylaminoethyl ketone,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , a colourless liquid (*hydrochloride*, needles, m. p. 140–141°; *picrate*, m. p. 136°; *oxime*, large needles, m. p. 104°). α-Piperidino-β-γ-diphenylpropane-γ-one,  $\text{C}_6\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{COPh}$ , (from deoxybenzoin, piperidine *hydrochloride*, and paraformaldehyde), a crystalline powder, m. p. 91° (the *hydrochloride* is very hygroscopic; *nitrate*, short needles, m. p. 117°). β-Tetrahydronaphthyl β-dimethylaminoethyl ketone (an-  
 nexed formula), a liquid (*hydrochloride*, needles, m. p. 170°; *picrate*,  
 needles, m. p. 156°). β-ar-

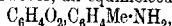


viscous liquid [*hydrochloride*, m. p. (anhydrous) 170°, (+aq.) 85°; *nitrate*, needles, m. p. 134–135°; *oxime hydrochloride*, silky needles, m. p. 211°].  
 H. W.

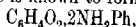
**The Influence of Substitution in the Components of Binary Solution Equilibria. XXXVII. The Systems of p-Benzoquinone with Phenols, Amines, and Hydrocarbons.** ROBERT KREMANN, SEPP SUTTER, FRANZ SITTE, HUBERT STRZELBA, and ALADAR DOBOTZKY (*Monatsh.*, 1922, 43, 269–313).—A systematic investigation has been made of the additive compounds of quinhydrone character formed by p-benzoquinone with a number of aromatic hydroxy-compounds, amines, and hydrocarbons. The method of attack adopted was through the determination of the condition-diagram of the binary system formed between p-benzoquinone and the substance under examination. Early experiments on these lines failed to give satisfactory results for two reasons. First, it was not realised that the additive compounds are not formed instantaneously when the two components are fused together, but frequently some considerable time at a higher temperature is needed to establish equilibrium. This phenomenon has not previously been recorded in the case of additive compounds between organic substances. Secondly, at the high temperatures at which fusion occurred, secondary reactions frequently started to some extent, rendering the observations worthless. The latter difficulty

was overcome by the addition to the binary system of a constant quantity of a third inactive substance, for which nitrobenzene was chosen. The ternary system could be treated as a quasi-binary system, and the nitrobenzene, by lowering the temperatures at which fusion and primary crystallisation took place, lessened the chance of the occurrence of secondary reactions between the *p*-benzoquinone and the other component. The existence of the following compounds between quinone and aromatic hydroxy-compounds was established from the occurrence of maxima in the *T-x* curves of the equilibrium diagrams: with phenol,  $C_6H_4O_2 \cdot 2PhOH$ ; with quinol,  $C_6H_4O_2 \cdot C_6H_4(OH)_2$ ; with pyrocatechol,  $2C_6H_4O_2 \cdot C_6H_4(OH)_2$ ; with resorcinol,  $2C_6H_4O_2 \cdot C_6H_4(OH)_2$ ; with pyrogallol,  $3C_6H_4O_2 \cdot C_6H_4(OH)_3$ .

These compounds can be explained on the assumption that combination takes place between the hydroxy-group and one of the two oxygen fields of force of the benzoquinone. In the cases of pyrocatechol, resorcinol, and pyrogallol, steric hindrance allows only one field of force of each benzoquinone molecule to come into play. The two naphthols both form, at first, equimolecular compounds,  $C_6H_4O_2 \cdot C_{10}H_7OH$ , but when the mixtures are heated for some time to a higher temperature, compounds of higher melting point containing two mols. of benzoquinone to one of naphthol are formed. This combination with a second molecule of benzoquinone must be attributed to the benzenoid fields of force. Of the three nitrophenols, 1:2:4-dinitrophenol, and picric acid, only *p*-nitrophenol forms a compound with quinone, the equimolecular compound,  $C_6H_4O_2 \cdot OH \cdot C_6H_4NO_2$ . Triphenylcarbinol forms no compound. Only three systems with amines were studied successfully. *p*-Toluidine, when carefully melted with *p*-benzoquinone, forms a simple mixture giving a eutectic; after warming the mixture some time, however, an equimolecular compound,



is formed. Since aniline is known to form the compound



it is evident that the *p*-methyl group has a similar effect on the combining power of aniline to the *p*-nitro-group on that of phenol.  $\alpha$ -Naphthylamine forms an equimolecular compound with *p*-benzoquinone, whilst  $\beta$ -naphthylamine, which at first forms no compound, when warmed for some time forms two compounds,  $C_6H_4O_2 \cdot C_{10}H_7NH_2$  and  $2C_6H_4O_2 \cdot C_{10}H_7NH_2$ . No compounds were detected between *p*-benzoquinone and any of the hydrocarbons triphenylmethane, naphthalene, acenaphthene, phenanthrene, fluorene, or with diphenylamine or carbazole, but anthracene forms an equimolecular compound.

E. H. B.

**The Catalytic Action of Mercury in the Sulphonation of Anthraquinone.** G. W. CLOUGH (*J. Soc. Dyers and Col.*, 1921, 38, 299–300).—After several attempts, the author has failed to confirm the statement of Martinef and Roux (*A.*, 1921, i, 732) that in the sulphonation of anthraquinone by means of fuming sulphuric acid in the presence of mercury as a catalyst, the  $\alpha$ -sulphonic acid

is always formed first and that this simultaneously changes into the  $\beta$ -isomeride.

A. J. H.

**Bromonitrocamphane.** P. M. GINNINGS and W. A. NOYES (*J. Amer. Chem. Soc.*, 1922, **44**, 2567—2573; cf. Forster, T., 1897, **71**, 199, 1030; 1899, **75**, 1141; 1900, **77**, 251; 1901, **79**, 108, 264, 644, 653, 987, 1003; 1902, **81**, 865; 1903, **83**, 78).—Further evidence is given in support of Forster's work on this subject, and definite proof of the structure of bromonitrocamphane anhydride is advanced.

On oxidation with nitric acid, bromonitrocamphane breaks down successively into camphor, camphoric acid, and camphoronic acid. The authors found no evidence of the formation of a hydrate of bromonitrocamphane, as suggested by Forster, during the action of potassium hypobromite on camphoroxime, but did find that a certain amount of hydroxynitrosocamphane was formed. The course of the action of the hypobromite is bromination of the camphoroxime and then oxidation to bromonitrocamphane. The anhydride of the last-named compound is best prepared by dissolving it in light petroleum of low boiling point and adding this to a mixture of concentrated sulphuric acid and light petroleum kept at  $-10^{\circ}$ . The anhydride reacts with Grignard's reagent to give *methylobromonitrocamphane anhydride*, m. p. 117—118°, which yields a *benzoyl* derivative, m. p. 113—114°, and is decomposed by alcoholic sodium hydroxide to give acetylcamphenylcarboxylic acid.

W. G.

**Preparation of Polycyclic Hydrocarbons of the Terpene Series.** CHEMISCHE FABRIK AUF ACTIEN (FORM. E. SCHERING) (D.R.P. 353933; from *Chem. Zentr.*, 1922, iv, 499).—Hydrazones of terpene ketones are heated with mercuric oxide in indifferent solvents; or the double salts of the hydrazones with mercuric chloride in the presence of an equivalent amount of alkali are heated in indifferent solvents. Slightly soluble basic mercury compounds are thereby formed which decompose on heating, as, for example,  $C_{10}H_{16} \cdot N \cdot NH \cdot Hg \cdot OH = C_{10}H_{16} + N_2 + Hg + H_2O$ .

*Tricyclene*, b. p. 153.5°, m. p. 63.5°, is formed from camphorhydrazone and mercuric oxide in alcohol after eight hours' heating. *d-Cyclofenchene*, from *d-fenchonehydrazone*, has b. p. 142.5—143.5°,  $d_D^{20}$  0.8588,  $n_D^{20}$  1.45134,  $[\alpha]_D^{20} +0.45^{\circ}$ . *apocyclene*, from camphenylhydrazone, has b. p. 138—139°, b. p. 120.5°/17 mm., m. p. 40.1°,  $d_D^{20}$  0.8694,  $n_D^{20}$  1.44914.

G. W. R.

**Oxidation of Sabinene with Chromyl Chloride.** GEORGE GERALD HENDERSON, JOHN MCGREGOR ROBERTSON, and DAVID CHRISTIE BROWN (T., 1922, **121**, 2717—2721).

**Constituents of some Indian Essential Oils.** JOHN LIONEL SIMONSEN and MADYAB GOPAL RAU (*Indian Forest Rec.*, 1922, **9**, 111—146).—I. The oleo-resin of *Pinus khasya* yields 57% of rosin. The turpentine essential oil has  $d_{20}^{20}$  0.8633,  $n_D^{20}$  1.4675, and  $[\alpha]_D^{20} +32.83^{\circ}$ . On distillation, it gives 70.6%, boiling at 153—155°, consisting of *d- $\alpha$ -pinene*, 11.7% at 159—169°, consisting of a

mixture of  $\alpha$ - and  $\beta$ -pinenes, and the higher fractions contain a terpene identical with *d*-longifolene.

II. The oleo-resin of *Pinus excelsa* yields about 68% of rosin. By fractionation of the oil, 87.9% of very pure *d*- $\alpha$ -pinene was obtained, together with *d*-terpineol, a bicyclic sesquiterpene, and a small quantity of a saturated hydrocarbon,  $C_{11}H_{24}$ , which appeared to be *n*-undecane. The turpentine itself had the constants  $d_{20}^{20}$  0.857,  $n_D^{20}$  1.4627, and  $[\alpha]_D^{20}$  +40.42°.

III. The essential oil from *Cedrus deodara*, Loudon, has already been examined by Roberts (T., 1916, 109, 791) and his results are in the main confirmed. The ketone present to the extent of 8–10% was definitely identified as 4-methyl- $\Delta^3$ -cyclohexenyl methyl ketone. The sesquiterpene (40%) was isolated as a colourless oil, b. p. 152–154°/40 mm.,  $d_{20}^{20}$  0.9195,  $n_D^{20}$  1.5040, and  $[\alpha]_D^{20}$  +13.86°. No crystalline derivatives could be obtained, and the substance was not identified. A sesquiterpene alcohol, b. p. 202–204°/55 mm., was also isolated in about 40% yield. It formed a viscid yellow oil,  $d_{20}^{20}$  0.9578,  $n_D^{20}$  1.515,  $[\alpha]_D^{20}$  +38.41. It gave no crystalline derivatives and could not be further characterised. No phenol, heptioic, or stearic acids were found, but the presence of esters of butyric, hexoic, and an unidentified crystalline acid, m. p. 110°, was confirmed.

IV. The essential oil from the grass *Andropogon Jwarancusa*, Jones (cf. T., 1922, 121, 2295), collected in Sind has a lower rotation ( $[\alpha]_D^{20}$  +42.8°), a higher density (0.9228), and a higher refraction ( $n_D^{20}$  1.4858) than that from grass of reputedly the same species grown in the Hazara district (cf. T., 1921, 119, 1645). It contains only 44% of piperitone, together with 24% of the terpene *d*- $\Delta^4$ -carene, identical with that in the Hazara oil, about 28% of a sesquiterpene alcohol, b. p. 176–177°/31 mm., 2% of an unidentified alcohol having an odour of roses, and small quantities of either free or combined palmitic, decoic, and octoic acids. The oil as a whole closely resembles that from *Cymbopogon Sennaarensis* described by Roberts (T., 1915, 107, 1465) rather than the Hazara oil.

V. The essential oil from the seeds of *Xanthoxylum alatum*, Roxb., contains more than 85% of *l*- $\alpha$ -phellandrene, together with a small proportion of linalool, and an unidentified sesquiterpene.

VI. The essential oil from the seeds of *Xanthoxylum acanthopodium*, DC. (yield 1.2%), had the following constants:  $d_{20}^{20}$  0.8837,  $n_D^{20}$  1.4746,  $[\alpha]_D^{20}$  +6.54°, saponification value 60.79, ditto after acetylation 242.5. The chief constituents are dipentene, methyl cinnamate, and more than 50% of linalool. In addition, *l*- $\alpha$ -phellandrene, a small quantity of an aldehyde or ketone, and a mixture of fatty acids consisting probably of hexoic, octoic, and heptioic acids were found.

VII. The essential oil from the seeds of *Xanthoxylum Budrunga*, Wall., is apparently identical with that examined by Semler (A., 1911, i, 1002) and stated by him to have been obtained from *X. alatum*. The terpene named by him xanthoxylene is definitely shown to be *L*-sabinene, as it gave sabinic acid, m. p. 55–57°, on oxidation, 1:4-terpin, on treatment with dilute sulphuric acid,

and terpinene dihydrochloride with hydrogen chloride in acetic acid solution. In addition to this hydrocarbon, terpinene was found in small quantities in the oil, together with an unidentified alcohol. No dimethoxyphloracetophenone could be found in the sample of oil examined.

G. F. M.

**Essential Oils.** SCHIMMEL & Co. (*Rep. Schimmel & Co.*, 1922, 5—166; from *Chem. Zentr.*, 1922, iv, 763—764).—Descriptions are given of a number of essential oils, many of which have already appeared. Essential oil from *Abies pindrow* (Indian silver fir) has  $d^{15}_4$  0.8647,  $[\alpha]_D -10^\circ 59'$ ,  $n_D^{20}$  1.47328, acid number 0.3; ester number 6.5. Indian baldrian oil has  $d^{15}_4$  0.9361,  $[\alpha]_D -34^\circ 6'$ ,  $n_D^{20}$  1.48712, acid number 37.3, ester number 39.8, acetyl number 69.1. Essential oil from *Erigeron canadense* has  $d^{15}_4$  0.8720,  $[\alpha]_D +53^\circ 56'$ ,  $n_D^{20}$  1.49922, acid number 0.3, ester number 63.5, acetyl number 70.3. Pine needle oil from *Tsuga canadensis* has (Cable, *J. Amer. Pharm. Assoc.*, 1921, 10, 170)  $d^{20}_4$  0.9020—0.9234,  $[\alpha]_D^{20} -14.80^\circ$  to  $21.65^\circ$ ,  $n_D^{20}$  1.4691—1.4704, acid number 0.33—0.71, ester number 103.8—147.35, acetyl number 113.5—171.94. Essential oil from *Tsuga heterophylla* has  $d^{20}_{15}$  0.8444—0.8521,  $[\alpha]_D^{20} -6^\circ$  to  $-20^\circ$ ,  $n_D^{20}$  1.4790—1.4840, acid number 2.57—3.4, ester number 6.7—17.25, acetyl number 19.6—33.4. Spanish oil of thyme has  $d^{15}_4$  0.9297,  $[\alpha]_D +0^\circ 35'$ ; it contains 45% of thymol, also amyl alcohol, amylcarbinols,  $\Delta^8$ -hexenol, and a new terpene,  $C_{11}H_{18}$ , of carrot-like odour, b. p. 155—156°, with  $d^{15}_4$  0.8533—0.8537,  $[\alpha]_D +4^\circ 35'$  to  $4^\circ 50'$ ,  $n_D^{20}$  1.46201—1.46231. The latter compound gives a nitrosochloride which decomposes at about 85°, a nitropiperidine, m. p. 194—195°, and a nitrolamine, m. p. 105—108°. The oil also contains camphene,  $\alpha$ -pinene,  $p$ -cymol,  $\gamma$ -terpinene, linalool,  $l$ -borneol,  $\psi$ -terpineol, geraniol, and caryophyllene. Essential oil from *Cicuta virosa*, L., has  $d^{15}_4$  0.8909,  $[\alpha]_D +16^\circ 32'$ ,  $n_D^{20}$  1.4848, acid number 3.7, ester number 17.7.

G. W. R.

**Caoutchouc.** RUDOLF PUMMERER and PETER A. BURKARD (*Ber.*, 1922, 55, [B], 3458—3472).—Caoutchouc dissolved in hexahydrotoluene has been submitted to catalytic hydrogenation in the presence of spongy platinum. In order to obtain a highly depolymerised and therefore highly active material, very dilute solutions (0.2—0.6%) are employed. The reaction occurs at the atmospheric temperature, but is more conveniently studied at 70—80° with freshly purified caoutchouc and recently prepared catalyst. With more concentrated solution (even 1%) the hydrogenation is frequently incomplete, possibly owing to poisoning of the catalyst by adsorbed caoutchouc. The caoutchouc absorbs one molecular proportion of hydrogen for each isoprene residue,  $(C_5H_8)_x + xH_2 = (C_5H_{10})_x$ , and there is no tendency towards further union with hydrogen after this stage is reached. If the caoutchouc molecule contained the isoprene residues in an open chain, a greater absorption of hydrogen would be expected in accordance with the scheme  $(C_5H_8)_x + (x+1)H_2 = C_{5x}H_{10x+2}$ . The accuracy attained in the experiments permits the conclusion to be drawn that caoutchouc consists either of a ring system or of an unusually long chain of

isoprene residues ( $x > 20$ ). The isolation of the hydrocaoutchouc from the solutions is somewhat difficult, since the product in substance and in solution is readily dehydrogenated to caoutchouc (at any rate in the presence of unavoidable traces of platinum). Precipitation of the colloid by kaolin in the absence of air and subsequent removal of the solvent under diminished pressure in an atmosphere of hydrogen yields *hydrocaoutchouc* as a very pale yellow, elastic skin, which swells and ultimately dissolves in ether and closely resembles ordinary caoutchouc. It certainly retains the high molecular weight.

The autoxidation of hydrocaoutchouc has been quantitatively studied by removing the excess of hydrogen by evacuation from the apparatus in which the substance has been prepared and subsequently agitating the solution with oxygen (in the presence of the platinum). A volume of oxygen, equal to half that of the hydrogen previously used, is rapidly absorbed, after which the action proceeds much more slowly and at approximately the same rate as observed with a similar solution of caoutchouc in hexahydrotoluene. The product of the autoxidation, *isocaoutchouc* II, when freshly prepared, dissolves easily and rapidly in ether without protracted swelling phenomena. When treated with hydrogen and spongy platinum, it rapidly absorbs one molecular proportion of the gas for each isoprene residue, thus showing that bridged linkings are not present in the molecule. In its solubility, *isocaoutchouc* II appears to be more closely allied to Harries's  $\alpha$ - and  $\beta$ -*isocaoutchouc* than to caoutchouc.

The absorption of gaseous oxygen by a very dilute solution of caoutchouc in hexahydrotoluene appears to be finished at the atmospheric temperature when a molecular proportion of oxygen has been used for every two isoprene residues. It is immaterial whether the action takes place in the presence or absence of spongy platinum. The tardiness with which absorption by concentrated solutions of caoutchouc occurs is very manifest.

The action of perbenzoic acid on solutions of caoutchouc in chloroform at  $0^\circ$  gives a viscous *caoutchouc oxide*,  $(C_8H_8O)_2$ , which is insoluble in all media. Products richer in oxygen are obtained in the presence of moisture. Reaction with the theoretical quantity of perbenzoic acid is almost complete after one hour, so that caoutchouc behaves normally towards this reagent.

The viscosity of a solution of caoutchouc in benzene at  $25^\circ$  is not changed if the solution is heated to gentle ebullition during eight hours and subsequently cooled rapidly or slowly to  $25^\circ$ ; if therefore a polymerisation equilibrium exists in caoutchouc solutions, it must be very rapidly attained. The coagulation of caoutchouc in boiling benzene is not observed with 2% solutions, but occurs slowly with 4% solutions. It does not take place during ten hours at  $50^\circ$ . The phenomenon is reversible.

H. W.

**Centaurein ; a New Glucoside obtained from the Roots of *Centaurea Jacea*.** MARC BRIDEL and CAMILLE CHARAUX (*Compt. rend.*, 1922, 175, 833—835).—*Centaurein*, a glucoside

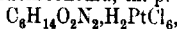
crystallising in small, pale yellow, elongated plates, of no definite m. p., was extracted from the dried roots of *Centaurea Jacea*. It contains 9.96% of water, which is lost at 50° in a vacuum, the glucoside itself remaining unchanged. It has  $[\alpha]_D -76.54^\circ$  ( $-85^\circ$  anhydrous) in methyl-alcoholic solution and  $[\alpha]_D -133.68^\circ$  ( $-148.47^\circ$  anhydrous) in 5% sodium hydroxide solution. Hydrolysis takes place slowly in boiling 5% sulphuric acid, the products being dextrose (33.68%) and *centaureidin* (70.77%), both of which were obtained in crystalline form.

H. J. E.

**Oxalyl Chloride in the Synthesis of the Triphenylmethane Dyes.** HARPER F. ZOLLER (*Science*, 1920, 52, 207).—Oxalyl chloride may be used instead of carbonyl chloride or Michler's ketone in the condensation of aniline and its derivatives, preferably in the presence of fused zinc chloride, for the production of triphenylmethane dyes.

A. A. E.

**$\delta$ -Methylornithine and  $\delta$ -Methylarginine. The Origin of Creatine.** IV. K. THOMAS, J. KAPFFHAMMER, and B. FLASCHEN-TRIGER (*Z. physiol. Chem.*, 1922, 124, 75—102).—Methylarginine, administered to rabbits, does not increase the total creatinine in the urine. The methylarginine required for the experiments was prepared from  $\delta$ -benzoylornithine (Sørensen, A., 1905, i, 600), which is obtained from ornithuric acid, but is contaminated with 3-benzoylamido-2-piperidone, long, white needles, m. p. 184°. On treatment with *p*-toluenesulphonyl chloride and alkali  $\delta$ -*p*-toluenesulphonyl- $\alpha$ -benzoylornithine,  $C_8H_7SO_2NH[CH_2]_3CH(NHBz)CO_2H$ , is formed, fine, white needles, m. p. 160—164° (decomp.). If too little alkali be used, 1-*p*-toluenesulphonyl-3-benzoylamido-piperidone, white needles, m. p. 184°, is obtained as a by-product. Methylation of  $\delta$ -*p*-toluenesulphonyl- $\alpha$ -benzoylornithine with methyl sulphate yields  $\delta$ -*p*-toluenesulphonyl- $\alpha$ -benzoyl- $\delta$ -methylornithine, needles, m. p. 188—189°. Hydrolysis of this compound with acid yields  $\delta$ -*p*-toluenesulphonyl- $\delta$ -methylornithine, thin plates, decomp. 245° (hydrochloride, glistening plates, m. p. 288°), whilst reduction with hydriodic acid and phosphonium iodide at 50—60° yields  $\alpha$ -benzoyl- $\delta$ -methylornithine,  $NHMe[CH_2]_3CH(NHBz)CO_2H$ , a microcrystalline white powder, m. p. 215°. On hydrolysis, dl-methylornithine is formed, isolated as the dihydrochloride, microcrystalline needles or crusts of rhombohedra, m. p. 157° (chloroplatinate,



m. p. 206°; monohydrochloride, m. p. 215—225°). Along with methylornithine is formed 3-amino-1-methyl-2-piperidone, isolated as the chloroplatinate,  $(C_8H_{12}ON_2)_2H_2PtCl_6$ , light yellow, rhombic leaflets, m. p. 210° (picrate,  $C_{12}H_{15}O_8N_5$ , m. p. 207°). The reaction of methylornithine and of aminomethylpiperidone with alkaloid precipitants has been investigated, with particular reference to Winterstein's isomeric lysine.

Treatment of methylornithine with a solution of cyanamide in presence of ammonia yields  $\alpha$ -benzoyl- $\delta$ -methylarginine, decomp. about 265°, and on hydrolysis with acid this yields dl-methylarginine,  $NH_2C(NH)NMe[CH_2]_3CH(NH_2)CO_2H$  [hydrochloride,

$C_7H_{16}O_2N_4 \cdot 2HCl$ , fine needles, aggregated in clumps, decomp.  $215^\circ$ ; *nitrate*,  $C_7H_{16}O_2N_4 \cdot 2HNO_3$ , rhombic prisms, m. p.  $153^\circ$ ; *cupri-nitrate*, fine, dark blue needles containing water of crystallisation, which on dehydrating have the formula  $(C_7H_{16}O_2N_4)_2 \cdot Cu(NO_3)_2$ ; *picrates*,  $C_7H_{16}O_2N_4 \cdot C_6H_3O_7N_3$ , felted needles, decomp.  $207-209^\circ$ , and  $C_7H_{16}O_2N_4 \cdot (C_6H_3O_7N_3)_2$ , m. p.  $145^\circ$ . *d*-Arginine also gives a *dipicrate*,  $C_6H_{14}O_2N_4 \cdot (C_6H_3O_7N_3)_2$ , m. p.  $198-199^\circ$ . Arginase does not act on methylarginine. W. O. K.

**The Reduction of Morphine by Emde's Method.** FRANZ FALTIS and THEODOR HECKZO (*Monatsh.*, 1922, 43, 255-267; cf. Faltis and Krausz, A., 1922, i, 676).—In the first part of the paper the influence of structure on the rupture of cyclic quaternary ammonium bases into tertiary bases by treatment with sodium amalgam (Emde's method, *loc. cit.*) is discussed. The course of the reaction is specially influenced, in condensed systems, by the position of a phenyl group in relation to the ring-nitrogen. In the previous paper the reaction was applied to dimethylpomorphine methochloride. It has now been extended to morphine itself in the form of dimethylmorphine methochloride. The product is identical with the  $\alpha$ -dimethylmorphimethine previously obtained by Pschorr (A., 1911, i, 908) by Hofmann's method. The rupture of the ring therefore takes place without reduction, and it is further shown that sodium amalgam has no reducing action on  $\alpha$ -dimethylmorphimethine methochloride. E. H. R.

**The Pilocarpine Series. I. Nitropilocarpine and Nitro-isopilocarpine.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], 31, 1027-1045; cf. Jowett, T., 1900, 77, 851; 1901, 79, 580 and 1331; 1903, 83, 438).—Whilst direct nitration of pilocarpine cannot be effected, the action of excess of concentrated sulphuric acid on pilocarpine nitrate gives an 80% yield of *nitropilocarpine*,  $NO_2 \cdot C_{11}H_{15}O_3N_2$ , hard, white, prismatic needles, m. p.  $135-136^\circ$ . The introduction of a nitro-group into the molecule causes pilocarpine to lose its basic character. The authors consider it probable that the entering group is attached to the 5-carbon atom in the iminazole ring. The substance is stable towards many reagents, and does not undergo isomerisation on being heated; it is attacked, however, by alkalis, being partly delactonised and partly isomerised, the change taking place very rapidly in cold alcoholic solution. The alkaline solution on acidification with acetic acid yields a white, crystalline precipitate of *nitropilocarpic acid*,  $NO_2 \cdot C_{11}H_{17}O_3N_2$ , m. p.  $199^\circ$ , which loses water on being heated at  $200-205^\circ$ , forming *nitropilocarpine*. The sodium and barium salts were prepared. Reduction of *nitropilocarpine* may be effected by various means; three molecules of hydrogen being utilised per molecule of alkaloid, but no reduction derivative was isolated. The stability of pilocarpine is considerably modified by introduction of the nitro-group; the nitro-derivative on prolonged boiling with excess of baryta water is decomposed with formation of barium cyanide and formate and the barium salts of pilopie and homopilopie acids, together with other

substances. The reaction is very complex owing to the formation of intermediate substances which react further, giving rise to secondary products. Pilopic and homopilopic acids may function either as monobasic, lactonic, or dibasic acids. Barium salts of the former type are obtained from the action of barium carbonate on the acid with subsequent filtration and evaporation to dryness, of the latter on heating the acid with baryta water, excess of which is eliminated with carbon dioxide. The constitution of pilocarpine is discussed but is not yet completely elucidated.

*Nitroisopilocarpine*, prepared similarly to nitropilocarpine, crystallises in small, white prisms, m. p.  $93-94^{\circ}$ , and forms salts with dilute alkalis, but is readily relactonised, yielding the original substance. Pilocarpine and isopilocarpine suffer similar decompositions with formation of the same products, but there is this difference, homopilopic acid appears to be formed in greater quantity from pilocarpine than is pilopic from nitropilocarpine; with the isomeride and its nitro-derivative the converse is the case. No evidence as to the nature of the isomerism was obtainable from the decomposition products, but it is pointed out that prolonged heating with baryta water may transform nitropilocarpine into its isomeride as a preliminary to decomposition. Both substances, however, yield methylamine at the outset, so that if isomerisation occurs, as suggested, the change affects, not the original substances, but their primary decomposition products.

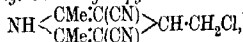
H. J. E.

**Phosphates of Strychnine.** J. BOUILLON (*J. Pharm. Chim.*, 1922, [vii], 26, 406—415).—Strychnine forms two phosphates by the direct union of the acid and the base under suitable conditions. The monobasic phosphate of the formula  $C_{21}H_{22}O_2N_2 \cdot H_3PO_4 \cdot 2H_2O$  was obtained by dissolving 3.34 g. of strychnine in 100 c.c. of water containing the calculated quantity of phosphoric acid. On cooling, the salt crystallised in fine needles. The dibasic salt,  $(C_{21}H_{22}O_2N_2)_2 \cdot H_3PO_4 \cdot 9H_2O$ , was obtained by combination of the theoretical amounts of strychnine and phosphoric acid in 80% alcohol. The hot solution slowly deposited the salt in glistening leaflets. It is but slightly soluble in water, and is partly dissociated by this solvent into the monobasic phosphate and free strychnine. It has  $[\alpha]_D -43.13^{\circ}$  in 80% alcohol. A tribasic phosphate could not be obtained, a solution of the acid and base in the requisite proportions depositing only crystals of the dibasic salt and strychnine.

G. F. M.

**Derivatives of Pyridine obtained from Diacetonitrile and Benzoacetodinitrile.** ERICH BENARY and GERTRUD LÖWENTHAL (*Ber.*, 1922, 55, [B], 3429—3434).—In a previous communication (Benary, A., 1921, i, 127), the transformation of ethyl 2:6-dimethyl-4-cyanomethyl-1:4-dihydropyridine-3:5-dicarboxylate into ethyl 5-methyl-3-cyanomethylpyrrole-2-carboxylate has been described. A number of compounds which might possibly suffer a similar conversion of the pyridine into the pyrrole ring have now been examined, but in no case has this change been observed, so that the reaction does not appear to be general.

Imidoacetoacetonitrile and  $\alpha\beta$ -dichloroethyl ether yield 2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile,

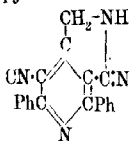


colourless leaflets, m. p.  $170^\circ$ , which is transformed by a solution of potassium cyanide in methyl alcohol into a mixture of 2:6-dimethyl-4-cyanomethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, colourless crystals, m. p.  $220^\circ$ , and (?) 2:6-dimethyl-4-carbamido-methyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, colourless leaflets, m. p.  $109^\circ$ . 2:6-Dimethyl-4-cyanomethylpyridine-3:5-dicarboxylonitrile, colourless leaflets, m. p.  $230^\circ$  (decomp.), is conveniently prepared by the action of sodium nitrite on a solution of the corresponding dihydro-compound in glacial acetic acid. The oxidation of 2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile to the pyridine derivative cannot be effected by reason of the unusual lability of the chlorine atom; the action of sodium nitrite on a solution of the compound in glacial acetic acid leads to the production of 3:5-dicyano-2:6-dimethyl-1:4-

dihydropyridine-4-aldoxime,  $\text{NH} \begin{array}{c} \text{CMe:C(CN)} \\ \text{CMe:C(CN)} \end{array} > \text{CH}\cdot\text{CH}\cdot\text{NOH}$ , prismatic needles, decomp.  $161^\circ$  after darkening at about  $157^\circ$ , which is further characterised by its conversion into a benzoate, colourless needles or leaflets, m. p.  $186^\circ$  after softening at  $176^\circ$ , and an acetate, long, colourless needles, m. p.  $115^\circ$ .

2:6-Diphenyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile,  $\text{NH} \begin{array}{c} \text{CPh:C(CN)} \\ \text{CPh:C(CN)} \end{array} > \text{CH}\cdot\text{CH}_2\text{Cl}$ , colourless leaflets, m. p.  $235^\circ$ , prepared from  $\alpha\beta$ -dichlorodiethyl ether and imidobenzoylacetonitrile, is not affected by sodium nitrite and glacial acetic acid, but is oxidised by nitric acid to 2:6-diphenyl-4-chloromethylpyridine-3:5-dicarboxylonitrile, long, colourless needles, m. p.  $177^\circ$ . The chlorodihydro-compound is converted by an alcoholic solution of potassium cyanide into 2:6-diphenyl-4-cyanomethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, pale brown leaflets, m. p.  $185^\circ$ .

Boiling aqueous potassium hydroxide solution converts 2:6-diphenyl-4-chloromethylpyridine-3:5-dicarboxylonitrile into 2:6-diphenyl-4-hydroxymethylpyridine-3:5-dicarboxylonitrile, colourless, slender needles, m. p.  $176^\circ$ , whereas alcoholic ammonia transforms it into a substance, pale brown needles, m. p.  $198^\circ$ , to which, on account of the absence of basic properties, the annexed constitution is ascribed.



H. W.

**Some  $\delta$ -Ketonic Nitriles and their Relation to Cyclic Compounds.** E. P. KOHLER, ALICE GRAUSTEIN, and D. R. MERRILL (*J. Amer. Chem. Soc.*, 1922, **44**, 2536—2556; cf. A., 1922, i, 461).—In the presence of a small amount of sodium methoxide and in very dry methyl alcohol, methyl cyanoacetate combines with  $\alpha\beta$ -unsaturated ketones and forms  $\gamma$ -ketonic nitriles. In indifferent media, these are rapidly converted by the action of halogen acids

into equilibrium mixtures containing small quantities of these nitriles mixed with isomeric tetrahydropyridine derivatives. This process takes place very rapidly, so that the open-chain compounds and their cyclic isomerides give the same products in reactions that take place in the presence of acids. Where bases are used, the products obtained from the two types are different. The cyclic compounds react very readily with the halogens and by alternately introducing halogen and eliminating halogen acid it is possible to go step by step from the tetrahydropyridine derivative to true pyridines. With the open-chain compounds, the action of halogens results in a mixture of a great number of open-chain and cyclic halogenated compounds, but the action can be controlled. Halogenation in the presence of potassium acetate gives open-chain compounds only, whilst the same process in glacial acetic acid gives mainly a true pyridine derivative. These reactions have been studied in the case of phenyl styryl ketone and *p*-chlorophenyl styryl ketone. The products from the two ketones behave alike, but the products from the chloro-derivatives generally are less fusible and less soluble than those from the chlorine-free substance.

Phenyl styryl ketone and methyl cyanoacetate condense together to give methyl  $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyrate,

$$\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me},$$

m. p.  $76^\circ$ , together with some of the trimolecular compound, m. p.  $220^\circ$ , formed by the addition of a second molecule of the unsaturated ketone. Methyl  $\alpha$ -cyano- $\gamma$ -*p*-chlorobenzoyl- $\beta$ -phenylbutyrate, m. p.  $126^\circ$ , and the trimolecular compound, m. p.  $230$ – $232^\circ$ , were similarly prepared. Using methyl  $\alpha$ -cyanopropionate instead of the cyanoacetate, the product in the latter case was methyl  $\alpha$ -cyano- $\gamma$ -*p*-chlorobenzoyl- $\beta$ -phenyl- $\alpha$ -methylbutyrate, in two stereoisomeric forms, m. p.  $108^\circ$  and  $92^\circ$ , respectively. When hydrolysed in acid medium the esters described above give ester acids, but when carefully hydrolysed with alcoholic potash the cyano-acid is the product. The compounds described are methyl hydrogen  $\gamma$ -benzoyl- $\beta$ -phenylethylmalonate, m. p.  $160^\circ$  (decomp.),  $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyric acid, m. p.  $160^\circ$  (decomp.), and  $\gamma$ -benzoyl- $\beta$ -phenylbutyronitrile, m. p.  $76^\circ$ , obtained by decomposing the latter at  $200^\circ$ .

The tetrahydropyridine derivatives described are methyl 6-keto-2:4-diphenyltetrahydropyridine-5-carboxylate, m. p.  $165$ – $166^\circ$ , and the free acid, m. p.  $130^\circ$  (decomp.); 6-keto-2:4-diphenyltetrahydropyridine, m. p.  $130^\circ$ ; methyl 6-keto-4-phenyl-2-*p*-chlorophenyltetrahydropyridine-5-carboxylate, m. p.  $204^\circ$ . On careful bromination, these tetrahydropyridine derivatives give monobromo-derivatives, but if the bromination is conducted at too high a temperature the product is contaminated with the corresponding dihydropyridine derivative. Methyl 3-bromo-6-keto-2:4-diphenyltetrahydropyridine-5-carboxylate had m. p.  $160$ – $161^\circ$ , and, on digestion with sodium methoxide in methyl alcohol, gives methyl 6-hydroxy-2:4-diphenylpyridine-5-carboxylate, the free acid of which has m. p.  $253^\circ$  (decomp.) and on heating at  $260^\circ$  decomposes, giving 6-hydroxy-2:4-diphenylpyridine. The monobromo-ester described above on further

bromination yields *methyl 3:5-dibromo-6-keto-2:4-diphenyltetrahydropyridine-5-carboxylate*, m. p. 160° (decomp.) and when a solution of this compound in dry methyl alcohol is rapidly saturated with hydrogen bromide it gives ammonium bromide, *methyl  $\alpha$ -dibromobenzoylphenylethylmalonate*, and *methyl  $\alpha$ -dibromo- $\gamma$ -benzoyl- $\beta$ -phenylethylmalonate*, m. p. 180°, an isomeride, m. p. 140°, of which was obtained during the earlier bromination. These two isomerides were decomposed on heating, giving *4-bromo-4-cyano-2-benzoyl-3-phenyltetrahydrofuran*, m. p. 275°. If the further bromination described above is carried out in boiling chloroform, the dibromo-compound loses hydrogen bromide and forms *methyl 3-bromo-6-hydroxy-2:4-diphenylpyridine-5-carboxylate*, m. p. 233—240°, which does not undergo further bromination, but gives a *perbromide*. The free acid has m. p. 270° (decomp.), and on heating gives *3-bromo-6-hydroxy-2:4-diphenylpyridine*. Similar bromination products from the *p*-chlorophenyl derivatives are *methyl 3-bromo-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*, m. p. 194°, *methyl 3:5-dibromo-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*, m. p. 183°, and *methyl 6-hydroxy-4-phenyl-2-p-chlorophenylpyridine-5-carboxylate*, m. p. 262°.

Bromination of the methyl cyanoacetate additive products in the presence of potassium acetate gave the following compounds: *methyl  $\alpha$ -bromo- $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyrate*, m. p. 130°; *methyl  $\alpha$ -dibromo- $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyrate*, m. p. 177—179°; *methyl  $\alpha$ -bromo- $\alpha$ -cyano- $\gamma$ -p-chlorobenzoyl- $\beta$ -phenylbutyrate*, in the form of two isomerides, m. p. 91—92° and 123°, respectively; *methyl  $\alpha$ -dibromo- $\alpha$ -cyano- $\gamma$ -p-chlorobenzoyl- $\beta$ -phenylbutyrate*, m. p. 193°. Products of bromination in glacial acetic acid are: *methyl 6-bromo-2:4-diphenylpyridine-5-carboxylate*, m. p. 147°, and its free acid, m. p. 206—208°; *methyl 6-bromo-4-phenyl-2-p-chlorophenylpyridine-5-carboxylate*, m. p. 106°.

Chlorination of the same additive products in chloroform solution gave excellent yields of open-chain substitution products. In this way, the authors prepared *methyl  $\alpha$ -chloro- $\alpha$ -cyano- $\beta$ -phenyl- $\gamma$ -p-chlorophenylbutyrate*, obtained in two stereoisomeric forms, m. p. 80° and 106°, respectively. A chloroform solution of the isomeride with the higher m. p. when saturated with hydrogen bromide and boiled for several hours gave a compound, m. p. 19° (decomp.), which is probably *methyl 5-chloro-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*. This ester reacts readily with chlorine and passes into *methyl 3-chloro-6-hydroxy-4-phenyl-2-p-chlorophenylpyridine-5-carboxylate*, m. p. 196°, and on further chlorination into *methyl 3:4:5-trichloro-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*.

cycloPropane derivatives are obtained by heating the  $\alpha$ -bromo-esters described above with potassium acetate in a suitable solvent; by removing hydrogen chloride from  $\alpha$ -chloro-compounds, or by eliminating bromine from  $\alpha$ -dibromo-compounds with potassium iodide. These processes gave stereoisomeric cyclopropane derivatives of which the following are described: *methyl 1-cyano-*

3-benzoyl-2-phenylcyclopropane-1-carboxylate, the three isomeric forms of which had m. p. 106°, 110°, and 178–180°, respectively; the free acid, m. p. 230° (decomp.), corresponding with these esters, and methyl 1-cyano-2-phenyl-3-p-chlorophenylcyclopropane-1-carboxylate, the two isomeric forms of which had m. p. 132° and 180°, respectively. W. G.

**$\alpha$ -Diketones of the Indole Group. I. G. SANNA** (*Gazzetta*, 1922, 52, ii, 165–170).—In addition to the products already described (Oddo and Sanna, A., 1922, i, 371), the action of oxalyl chloride on magnesium indolyl bromide yields 2:2-indil, 2:3-indil, and 1:2-indil; 3:3-indil is also formed in traces, in some cases, but not at all in others.

3:3-Indilphenylosazone,  $[\text{C}_8\text{H}_6\text{N}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot]_2$ , crystallises in yellow prisms, m. p. 158° (decomp.), and when heated with alcohol and ferric chloride undergoes oxidation to the corresponding osotetrazone.

2:3-Di-3'-indolylquinoxaline,  $\text{C}_8\text{H}_4 \begin{smallmatrix} \text{N}:\text{C}-\text{C}_6\text{H}_5\text{N} \\ \text{N}:\text{C}-\text{C}_6\text{H}_5\text{N} \end{smallmatrix}$ , obtained by the condensation of 3:3-indil with *o*-phenylenediamine, forms masses of brick-red prisms, m. p. 163° (decomp.), and gives the general reactions of the quinoxalines.

3:3-Indil forms a silver derivative,  $\text{C}_{18}\text{H}_{10}\text{O}_2\text{N}_2\text{Ag}_2$ , as a grey precipitate, and yields indole-3-carboxylic acid when oxidised by means of hydrogen peroxide.

2:2-Indil (2:2-di-indolyl),  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_2$ , forms pale yellow, tabular prisms, m. p. 273°, and has the normal molecular weight in freezing acetic acid. The phenylosazone,  $\text{C}_{30}\text{H}_{24}\text{N}_6$ , crystallises in yellow, tabular prisms, m. p. 170° (decomp.), and is oxidised by ferric chloride to the corresponding osotetrazone. When oxidised by means of hydrogen peroxide or fused with potassium hydroxide, 2:2-indil yields indole-2-carboxylic acid.

2:3-Di-2'-indolylquinoxaline,  $\text{C}_{24}\text{H}_{16}\text{N}_4$ , crystallises in tufts of red, acicular prisms, m. p. 154° (decomp.), and shows the general reactions of the quinoxalines.

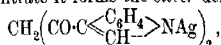
Bis-1:2-indil (bis-1:2-di-indolyl) (annexed formula), also obtained from the products of the action of oxalyl chloride on magnesium indolyl bromide, crystallises in yellow scales, m. p. 320°; when heated in a reflux apparatus with concentrated potassium hydroxide, it yields 2:2-indil, and when fused with potassium hydroxide, indole-2-carboxylic acid.

A compound, forming white crystals, m. p. 163°, also occurs among the products of the reaction, but has not been characterised. T. H. P.

**Syntheses of  $\beta$ -Diketones in the Indole Group. I. G. SANNA** (*Gazzetta*, 1922, 52, ii, 170–176).—The action of malonyl chloride on magnesium indolyl bromide proceeds similarly to that on magnesium pyrrol bromide (Oddo and Dainotti, A., 1912,

i, 721) and yields di-3-indoylmethane. In many of its reactions this compound behaves, like all  $\beta$ -diketones, as a hydroxy-ketone, but in the solid state and also in solution it appears to exist principally in the normal diketonic form, being transformed, slowly at the ordinary temperature but rapidly when heated, into the keto-enolic modification. Attempts to separate the two tautomeric forms were unsuccessful, but indicated great stability in the normal modification. Since only the 3:3'-compound was obtained in the above reaction, the greater length of the chain in malonyl chloride appears to enhance the tendency to attack in the position of the indole nucleus most remote from the imino-group.

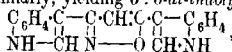
Di-3-indoylmethane,  $\text{CH}_2(\text{CO}-\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{>NH})_2$ , crystallises in cotton-like masses of minute, white needles, blackening at about  $230^\circ$ , m. p.  $287^\circ$  (decomp.), and is highly resistant to the action of alkali hydroxide or concentrated sulphuric acid. In alcoholic solution it gives with ferric chloride an immediate emerald-green coloration, which tends to darken and to assume a violet reflection. With cupric acetate in alcoholic solution, it gives a greenish-yellow liquid which, on cooling, deposits the copper salt,  $(\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2)_2\text{Cu}$ , crystallising in brownish-red prisms, m. p.  $254^\circ$  (decomp.). With ammoniacal silver nitrate it forms the silver derivative,



as a white, curdy precipitate; the formation of this compound shows that the hydrogen replaced by the chain is not the imine hydrogen. Hydrolysis of di-indoylmethane by means of alkali hydroxide yields indole-3-carboxylic acid and 3-indolyl methyl ketone (3-acetylindole).

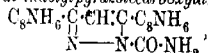
Di-indoylmethane reacts readily with phenylhydrazine, giving the dehydration product of the monophenylhydrazone, namely, 1-phenyl-3:5-di-indolylpyrazole,  $\begin{smallmatrix} \text{C}_6\text{H}_4 & \text{C} & \text{C} & \text{CH} & \text{C} & \text{C} & \text{C}_6\text{H}_4 \\ | & | & | & | & | & | \\ \text{NH} & \text{CH} & \text{N} & \text{---} & \text{NPh} & \text{CH} & \text{NH} \end{smallmatrix}$ , which

crystallises in yellow prisms resembling knife-blades, m. p.  $236^\circ$  (decomp.), and is converted into the corresponding pyrazoline base when reduced by means of sodium. The reaction with hydroxylamine proceeds similarly, yielding 3:5-di-indolylisooxazole,



which crystallises in yellow prisms, m. p.  $219^\circ$  (decomp.), and exhibits feebly basic properties; restriction of the action of the hydroxylamine results in the formation of a compound which crystallises in slender, red needles, m. p. about  $170^\circ$  (decomp.), and is possibly the mono-oxime of the diketone, as it exhibits reducing properties and yields di-indoylmethane when boiled with dilute hydrochloric acid.

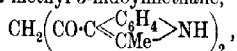
Condensation of di-indoylmethane with semicarbazide results in the formation of di-indolylpyrazolecarboxylamide,



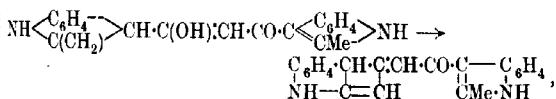
which then takes up a molecule of water and loses ammonia and carbon dioxide, giving 3:5-di-indolylpyrazole,  $\text{C}_8\text{NH}_8 \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{C}_8\text{NH}_8$ ,  $\begin{smallmatrix} \text{N} & \text{---} & \text{NH} \\ | & & | \end{smallmatrix}$ , which forms yellow crystals, m. p. 229° (decomp.), and on reduction with sodium yields the corresponding pyrazoline; the latter, like 1-phenyl-3:5-di-indolylpyrazole, gives a violet coloration with sulphuric acid and potassium dichromate, and a bright purple coloration with nitrous acid.

T. H. P.

**Syntheses of  $\beta$ -Diketones in the Indole Group. II. G. SANNA** (*Gazzetta*, 1922, 52, ii, 177—184; cf. preceding abstract).—The action of malonyl chloride on magnesium 2-methylindolyl bromide yields di-2-methyl-3-indolylmethane,



which is closely analogous to its lower homologue and exhibits all the reactions characteristic of the  $\beta$ -diketones. It dissolves readily in cold alkali hydroxide solution and is reprecipitated unchanged on addition to the solution of dilute sulphuric acid. With ferric chloride, its alcoholic solution gives an intense emerald-green coloration quickly changing to violet. When boiled with alkali hydroxide solution it gives 2-methylindole-3-carboxylic acid and 2-methyl-3-indolyl methyl ketone, and with phenylhydrazine, hydroxylamine, and semicarbazide it reacts similarly to the lower homologue. The above compound, which must be regarded as the hydroxyketonic form,  $\cdot \text{C} \cdot \text{C}(\text{OH}) \cdot \text{CH} \cdot \text{CO} \cdot$ , is accompanied by an isomeride which is insoluble in alkali hydroxide solution, yields no coloration in the cold with ferric chloride, is not precipitated by cupric acetate or esterified by phenylcarbimide, and appears to be the normal diketonic form containing the grouping  $\cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot$ . In addition to these two compounds, a third, which is formed in small proportion, has the composition of an anhydro-compound and may be formed by dehydration of the mixed keto-enolic modification:



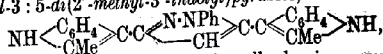
or may represent the result of condensation between the dimethylindolylmethane (1 mol.) and 2-methylindole (2 mols.).

Di-2-methyl-3-indolylmethane crystallises in yellow, rhomboedral plates, m. p. 219°, and has the normal molecular weight in freezing acetic acid. The hydroxy-ketonic tautomeride forms a yellow, microcrystalline powder or prismatic rods, m. p. 219°, and has the calculated molecular weight in freezing acetic acid, but differs from the preceding compound in its solubility in organic solvents.

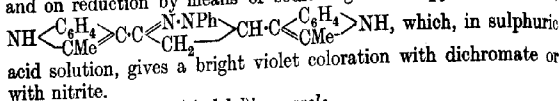
From the latter compound the following derivatives are obtainable. The cupric derivative,  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2\text{Cu}$ , forms a yellow powder

or octahedra with violet reflection, m. p. 220° (decomp.); the silver derivative,  $C_{21}H_{18}O_2N_2Ag_2$ , was also prepared.

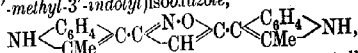
1-Phenyl-3 : 5-di(2'-methyl-3'-indolyl)pyrazole,



obtained by condensation with phenylhydrazine, crystallises in serrate aggregates of pale yellow prisms, m. p. 192° (decomp.), and on reduction by means of sodium gives the pyrazoline base,

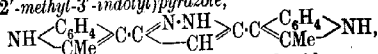


3 : 5-Di(2'-methyl-3'-indolyl)isoxazole,



prepared by the action of hydroxylamine, crystallises in pale yellow prisms, m. p. 174° (decomp.), and exhibits basic properties more marked than those of the corresponding indole derivative; its hydrochloric acid solution is rendered turbid by ammonia, platinum chloride, or auric chloride.

3 : 5-Di(2'-methyl-3'-indolyl)pyrazole,



obtained by condensation with semicarbazide, crystallises in minute, yellow needles, m. p. 247° (decomp.), and is reduced by sodium to the corresponding pyrazoline derivative, which yields violet colorations when treated in sulphuric acid solution with dichromate or sodium nitrite.

The anhydro-compound (see above),  $C_{21}H_{18}O_2N_2 \cdot H_2O$ , forms short, stout, yellow, hexagonal prisms, m. p. 224° (decomp.).

T. H. P.

### Conversion of $\beta$ -Phenylhydroxylamine into Quinoline Bases.

E. BAMBERGER and H. WEITNAUER (*Ber.*, 1922, 55, [B], 3376—3382).—Quinoline is prepared in very small yield by the action of glycerol and sulphuric acid on  $\beta$ -phenylhydroxylamine (cf. Hindermann, *Diss. Zurich*, 1897). Replacement of glycerol by acetaldehyde, which is generally assumed to be an intermediate product in Skraup's synthesis of quinoline, leads to slightly better results. The intermediate *nitron*,  $O:NPh:CH:CH:CH_2$ , could only be isolated in an impure, amorphous, resinous form; when heated at a relatively somewhat high temperature and subsequently treated with dilute sulphuric acid, it gives quinoline in quantity which never exceeds 5% of that theoretically possible. Crotonaldehyde and  $\beta$ -phenylhydroxylamine give 2-methylquinoline. Cinnamaldehyde condenses with phenylhydroxylamine to give phenylacryl-*N*-phenylnitron,  $O:NPh:CH:CH:CHPh$ , yellow needles, m. p. 155—156°, when rapidly heated, which is transformed by a little concentrated sulphuric acid in the presence of glacial acetic acid into 2-phenylquinoline, m. p. 82.5—83°.

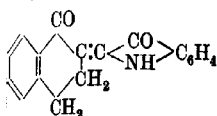
The present synthesis differs from that of Skraup in that it is

not necessary to provide an external source of the necessary oxygen atom, the latter being contained in the phenylhydroxylamine.

H. W.

**Reactivity of Methyl Groups in Heterocyclic Bases.** WILLIAM HOBSON MILLS and JAMES LEONARD BRIERLEY SMITH (T., 1922, 121, 2724—2737).

**Dyes Derived from  $\alpha$ -Ketotetrahydronaphthalene [ $\alpha$ -Tetra-  
lone].** WALTER HERZOG and J. KREIDL (Ber., 1922, 55, [B],  
3394—3400).—2-Tetrahydronaphthalene-2'-indoleindigotin [1-Keto-  
2:(2')-indoxyltetrahydronaphthalene] (annexed formula) is obtained



when equivalent quantities of  $\alpha$ -keto-  
tetrahydronaphthalene and  $\alpha$ -isatinil  
are heated under a reflux condenser in  
the presence of light petroleum (b. p.  
150—200°). It forms bluish-violet  
crystals with a bronze reflex, decomp.

about 250°. It is transformed by fuming sulphuric acid into  
sulphonic acid which gives a pure blue solution in water.  
With alkali and hyposulphite, it yields a yellow vat from which  
wool and cotton are dyed in pure blue tones. 1-Keto-2:3'-oxy-  
thionaphthentetrahydronaphthalene, reddish-violet needles, de-  
comp. about 250°, is prepared by the action of 2-ketotetra-  
hydronaphthalene on  $\alpha$ -thionaphthenquinoneanil in boiling acetic  
anhydride solution. It is sulphonated by fuming sulphuric acid.  
With alkali and hyposulphite, it gives a greenish-yellow vat  
from which wool is dyed in dark brownish-violet, cotton in reddish-  
violet shades. Attempts to condense  $\alpha$ -ketotetrahydronaphthalene  
with  $\beta$ -isatinil were unsuccessful.

$\alpha$ -Ketotetrahydronaphthalene reacts with terephthalaldehyde in  
alcoholic solution in the presence of sodium hydroxide to yield  
the compound  $C_6H_4 \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \cdot C_6H_4 \cdot \text{CH} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \cdot C_6H_4 \cdot \text{CH} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} C_6H_4$ , straw-  
yellow crystals, m. p. (indefinite) 240—255° after darkening at 230°,  
from which a vat could not be obtained.  $\alpha$ -Ketotetrahydronaph-  
thalene, terephthalaldehyde, and 3-hydroxythionaphthen yield  
mainly a substance, small golden-yellow needles, m. p. 192—193°  
the constitution of which has not yet been elucidated), and in

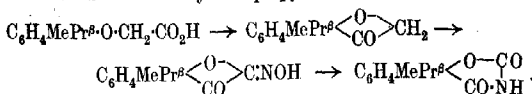
minor amount the dye  $C_6H_4 \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \cdot C_6H_4 \cdot \text{CH} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} C_6H_4$ .

Cinnamaldehyde and  $\alpha$ -ketotetrahydronaphthalene yield  $\beta$ -cinn-  
mylidene- $\alpha$ -ketotetrahydronaphthalene,  $C_6H_4 \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \cdot C_6H_4 \cdot \text{CH} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} C_6H_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CHPh}$ ,  
large, yellow leaflets, m. p. 132—134°, which becomes polymerised at  
220—230°.

H. W.

**1:3-Benzoxazine. I. Conversion of Oximinocoumaran-  
ones into 1:3-Benzoxazine Derivatives.** EFISIO MAMELI  
Gazzetta, 1922, 52, ii, 184—189).—4-Methyl-7-isopropyl-3-coumar-  
anone, obtained from thymoxyacetic acid, when treated with  
nitrous acid, gives 2-oximino-4-methyl-7-isopropylcoumaranone,

which is converted by the action of phosphorus pentachloride into 2:4-diketo-5-methyl-8-isopropyl-1:3-benzoxazine:



This reaction represents the ordinary Beckmann transposition of the type  $\text{R}\cdot\text{C}\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NOH} \end{array}\text{R}' \rightarrow \text{R}\cdot\text{C}\begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{CO}\cdot\text{R}' \end{array} \rightarrow \text{R}\cdot\text{C}\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{NH}\cdot\text{CO}\cdot\text{R}' \end{array}$  which

has been observed, together with that of the type  $\text{R}\cdot\text{C}\begin{array}{c} \text{CO}\cdot\text{R}' \\ \diagup \quad \diagdown \\ \text{NOH} \end{array} \rightarrow$

$\text{R}\cdot\text{C}\begin{array}{c} \text{COR}' \\ \diagup \quad \diagdown \\ \text{N} + \text{OH} \end{array}$ , with certain other nitrosoketones. The action of phos-

phorus pentachloride on cyclic oximinoketones, such as oximinocamphor and oximinohydrindones, results in the opening of the nucleus. The above transposition is the first observed instance of the transformation of a pentagonal furan ring into a hexagonal oxazine ring. The constitution of 2:4-diketo-5-methyl-8-isopropyl-1:3-benzoxazine is confirmed by its conversion, when heated with dilute aqueous or alcoholic sodium hydroxide solution, into *o*-thymotamide, which was prepared also by the action of ammonia on ethyl thymotate.

2:3-Diketo-5-methyl-8-isopropyl-1:3-benzoxazine,  $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}$ , crystallises in a mass of slender, white needles or scales, m. p. 152–153°, decomposing at 177°, and with ferric chloride in either aqueous or benzene solution gives no coloration in the cold and a straw-yellow coloration when heated; it yields no coloration with concentrated sulphuric acid and is not precipitated by picric acid in alcoholic solution. The potassium salt,  $\text{C}_{12}\text{H}_{12}\text{O}_3\text{NK}$ , forms a voluminous, white precipitate, the methyl ester, white needles, m. p. 129°, and the ethyl ester, a white, crystalline powder, m. p. 104°.

*o*-Thymotamide,  $\text{OH}\cdot\text{C}_6\text{H}_4\text{MePr}^s\cdot\text{CO}\cdot\text{NH}_2$ , forms bundles of white needles, m. p. 137°, decomposing at 205°, and gives with ferric chloride a blue coloration in aqueous solution and a green or violet coloration, changing to reddish-violet when heated in benzene solution. It remains unchanged when boiled with concentrated hydrochloric acid, gives no coloration with sulphuric acid, and is not precipitated by picric acid in alcoholic solution. T. H. P.

**Dyes derived from *xx'*-Dicyanodibenzyl Diketone.** SIKH-BHUSHAN DUTT and NIRMAL KUMAR SEN (T., 1922, 121, 2663–2667).

**The Substituted Thiocarbamides. III. The Synthesis of Thiazolidine and Thiazan Derivatives.** F. B. DAINS, R. Q. BREWSTER, J. S. BLAIR, and W. C. THOMPSON (*J. Amer. Chem. Soc.*, 1922, 44, 2637–2643).—Arylallyl amines react with thiocarbimides to give  $\alpha$ -allyl- $\alpha$ , $\beta$ -diarylthiocarbamides, and these, by the action of acetyl chloride or on heating with hydrochloric acid, suffer rearrangement to 2:3-disubstituted thiazolidines. The

following are described.  $\alpha\beta$ -Diphenyl- $\alpha$ -allylthiocarbamide, m. p. 111°;  $\alpha$ -phenyl- $\beta$ -p-bromophenyl- $\alpha$ -allylthiocarbamide, m. p. 123°;  $\alpha$ -phenyl- $\beta$ -p-tolyl- $\alpha$ -allylthiocarbamide, m. p. 107°;  $\beta$ -phenyl- $\alpha$ -p-tolyl- $\alpha$ -allylthiocarbamide, m. p. 91.5°;  $\beta$ -p-bromophenyl- $\alpha$ -p-tolyl- $\alpha$ -allylthiocarbamide, m. p. 121°;  $\alpha\beta$ -di-p-tolyl- $\alpha$ -allylthiocarbamide, m. p. 113°; 2-phenylimino-3-phenyl-5-methylthiazolidine, n. p. 98°, and its *picrate*, m. p. 168—169°; 2-p-bromophenylimino-3-phenyl-5-methylthiazolidine, m. p. 106°; 2-p-tolylimino-3-phenyl-5-methylthiazolidine, an oil, and its *picrate*, m. p. 188°; 2-phenylimino-3-p-tolyl-5-methylthiazolidine, m. p. 72—73°, and its *picrate*, n. p. 164—166°; 2-p-bromophenylimino-3-p-tolyl-5-methylthiazolidine, m. p. 81°, and 2-p-tolylimino-3-p-tolyl-5-methylthiazolidine, an oil, and its *picrate*, m. p. 140°.

Arylaminoethanols were also found to unite with arylthiocarbamides and arylcarbimides, and the resulting thiocarbamides and carbamides either by the action of heat alone or under the influence of halogen acids lost water and formed thiazolidines and oxazolidines of known structure. New compounds thus prepared are 2-o-tolylimino-3-phenylthiazolidine, m. p. 94°; 2-p-tolylimino-3-phenylthiazolidine, m. p. 113°; 2-phenylimino-3-o-tolylthiazolidine, m. p. 92°; and 2-phenylimino-3-phenyloxazolidine, m. p. 124°. In a similar manner, the arylaminopropanols gave thiocarbamides, which, under the influence of acids, condensed to a six-membered thiazan ring. The arylpropanols were obtained by heating trimethylene chlorohydrin with the amine for several hours at 130°. Thus *p*-tolylamine gave *p*-tolyl- $\gamma$ -hydroxypropylamine. Thiocarbamides and thiazans thus prepared are  $\alpha\beta$ -diphenyl- $\alpha$ -propanolthiocarbamide, m. p. 130°; 2-phenylimino-3-phenylthiazan, m. p. 139°;  $\alpha\beta$ -di-p-tolyl- $\alpha$ -propanolthiocarbamide, m. p. 142°; 2-p-tolylimino-3-p-tolylthiazan, m. p. 111°;  $\beta$ -phenyl- $\alpha$ -p-tolyl- $\alpha$ -propanolthiocarbamide, m. p. 146°;  $\alpha$ -phenyl- $\beta$ -p-tolyl- $\alpha$ -propanolthiocarbamide, m. p. 127°; 2-phenylimino-3-p-tolylthiazan, m. p. 139°, and 2-p-tolylimino-3-phenylthiazan, m. p. 94°.

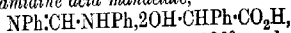
$\gamma$ -Chloro- $\alpha$ -arylamino- $\beta$ -hydroxypropanes combined with thiocarbimides to give thiocarbamides, which could not be isolated, owing to loss of hydrogen chloride and the consequent closure of the thiazan ring with the production of 5-hydroxythiazans, of which the following are described. 2-Phenylimino-5-hydroxy-3-p-tolylthiazan, m. p. 175°; 2-p-tolylimino-5-hydroxy-3-p-tolylthiazan, m. p. 142°, and its *hydrochloride*, m. p. 204°, and *picrate*, n. p. 195°; 2-phenylimino-5-hydroxy-3-*p*-anisylthiazan, m. p. 157°, and its *picrate*, m. p. 135°; 2-phenylimino-5-hydroxy-3-*p*-chlorophenylthiazan, m. p. 171°; 2-phenylimino-5-hydroxy-3-phenylthiazan, n. p. 175°, and its *picrate*, m. p. 150°, and *phenylurethane* derivative, m. p. 185°.

W. G.

**Isonitriles. IV. Reaction with Organic Acids.** M. PASERINI (*Gazzetta*, 1922, 52, ii, 250—257; cf. A., 1921, i, 743, 895; 1922, i, 731).—At the ordinary temperature, aromatic isonitriles [carbalamines] react with certain organic acids yielding carbon monoxide and salts of substituted formamides. Thus, with benzoic,

mandelic, lactic, and salicylic acids, phenylcarbylamine gives salts of diphenylformamidine composed of two mols. of the acid and one mol. of the base. Acetic acid, however, yields, not diphenylformamidine, but a syrupy liquid probably containing formanilide and possibly also acetanilide. From *p*-carbylaminoazobenzene and lactic acid, the acid lactate of 4:4'-bisazobenzeneformamidine is obtained, together with formyl-*p*-aminoazobenzene. The arylformamidine salts formed in these reactions are accompanied by oily compounds which yield aniline and alkali formates when heated with alkali hydroxide and are probably formanilides. According to Nef (A., 1892, 1438), the action of hydrogen chloride on phenylcarbylamine in anhydrous ethereal solution yields the additive compound  $(NPh\cdot CHCl)_2\cdot HCl$ . The formation of this compound is not detectable, although it may occur as an intermediate stage, in the action of hydrogen chloride and acetone or methyl ethyl ketone on phenylcarbylamine or *p*-carbylaminoazobenzene, the only products observed being the monohydrochlorides of the corresponding arylformamidines. Thus, hydrochloric acid in presence of ketones acts like organic acid in absence of ketones or aldehydes.

*Diphenylformamidine acid mandelate*,



crystallises in colourless needles, m. p. 126°, and, when suspended in water, yields part of its acid to the latter. The *acid lactate*,  $C_{13}H_{12}N_2\cdot 2C_3H_5O_3$ , forms long, colourless needles, m. p. 136°, and when treated with water, yields the *normal lactate*, which crystallises in colourless needles, m. p. 151°. *Diphenylformamidine salicylate* crystallises in large plates, m. p. 165°, softening at 160°, and the *benzoate* in colourless needles, m. p. 175–176°.

4:4'-*Bisazobenzeneformamidine acid lactate*,  $C_{25}H_{20}N_6\cdot 2C_3H_5O_3$ , crystallises in flat, orange needles, m. p. 153°, and the *free base*,  $C_{25}H_{20}N_6$ , in lustrous, orange needles, m. p. 196–197°.

Diphenylformamidine picrate,  $C_{13}H_{12}N_2\cdot C_6H_3O_7N_3$ , is formed by the action of picric acid on phenylcarbylamine. T. H. P.

**The Additive Formation of Four-membered Rings. I. The Synthesis and Division of Derivatives from 1:3-Dimethindiazidine.** CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (T., 1922, 121, 2793–2804).

**Barbituric Acid.** WALTER BOCK (Ber., 1922, 55, [B], 3400–3405).—An aqueous solution of barbituric acid gives a bright yellowish-red coloration with a piece of wood. The reaction is shown distinctly at a dilution of 1 in 1000; it is not disturbed by the presence of free mineral acids. Barbituric acids, substituted in position 5, do not appear to give the reaction.

5-Bromobarbituric acid, decomp. 212–215° after previous softening, can be prepared directly from the parent acid dissolved in water and bromine (four-fifths molecular proportion) at 50–60°. It is transformed by further treatment with bromine into 5:5-dibromobarbituric acid, prisms, decomp. 220–221°, or leaflets, decomp. 235–237°, which appear to be chemically identical. The

prismatic form is also obtained by the action of bromine on benzylidenebarbituric acid. Whereas the salts of monobromobarbituric acid are stable towards water, the free acid is readily decomposed, yielding mainly hydurilic acid; barbituric acid is also produced, but the presence of parabanic acid could not be established with certainty. 5:5-Dibromobarbituric acid is not greatly affected by a short treatment with boiling water, but by longer action is converted into alloxan and ultimately into hydurilic and barbituric acids; since the latter may be regarded as reduction products of alloxan it appears that other substances arising from the simultaneous oxidation of another part of the latter must also be present.

Aqueous solutions of barbituric acid and *p*-benzoquinone give an intense dark red colour which is perceptible at a dilution of 1 in 10,000. When equivalent proportions of the components are used, a definite product cannot be isolated and the colour disappears after short boiling. When, however, the acid and benzoquinone are taken in the molecular proportion 1:2, a tribasic acid,  $C_{26}H_{20}O_{15}N_4$ , an amorphous, black powder which decomposes without melting when heated, is obtained (the barium salt was analysed). The quinone appears to act to some extent as an oxidising agent.

H. W.

**Nitroso-2-hydroxyindazole.** E. BAMBERGER (*Ber.*, 1922, 55, [B], 3371—3375).—In a previous communication, Bamberger and Demuth (*A.*, 1902, i, 650) have shown that 2-hydroxyindazole is obtained by the action of alkali hydroxide on *o*-azidobenzaldoxime, and is converted by nitrous acid into a nitroso-derivative. The latter compound is now proved to be 3-nitroso-2-hydroxyindazole,  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{C}(\text{NO}) \end{smallmatrix} \text{N-OH}$  or  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{C}(\text{NO}) \end{smallmatrix} \text{N-OH}$ , since it is converted by reduction with tin foil in the presence of glacial acetic acid into 3-aminoindazole, m. p. 153—154°.

Preliminary experiments appear to show that *o*-hydroxylaminobenzaldoxime is not transformed into 2-hydroxyindazole by the action of alcoholic potash at the atmospheric temperature.

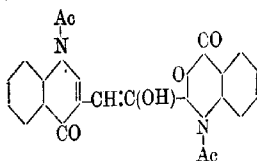
H. W.

**Catalytic Reduction of Indigotin.** ANDRÉ BROCHET (*Rev. Gen. Mat. Col.*, 1922, 27, 131—136).—Indigotin is rapidly reduced to indigo-white by hydrogenation even at atmospheric pressures, in presence of a reduced nickel catalyst, particularly at slightly elevated temperatures, as, for example, 50—60°, and in presence of sodium hydroxide. The catalyst is added to a suspension of about twice its weight of indigotin in dilute sodium hydroxide solution, and the gas is either bubbled through the liquid with vigorous agitation, or the liquid may be shaken in an atmosphere of the gas. Reduction is complete in one half to one hour, and the nickel recovered from the bleached indigo solution by filtration may be used repeatedly for subsequent hydrogenations. The catalyst retains its activity unimpaired for long periods. Other vat dyes such as "thioindigo," indanthrene, etc., and also certain

dyes which are not reoxidised by air, such as malachite-green, can in a similar way be converted into their leuco-compounds.

G. F. M.

**The Action of Acetic Anhydride on some Furfurylidene-anthranilic Acids.** JOHN B. EKELEY and EMMET C. ROGERS (*J. Amer. Chem. Soc.*, 1922, **44**, 2655—2657).—Furfurylideneanthranilic acid, m. p. 151° (decomp.) when heated in xylene with excess of acetic anhydride, gave as a final product a compound, m. p. 208°, which is probably the enol form of 1-keto-4-acetyl-3(4': keto-1'-acetyldihydro-2-quinolylacetyl)-dihydro-2:4-benzoxazine (annexed formula). It is probable



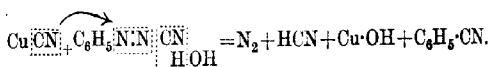
that in the first stage of the reaction a furfuryloxazine is formed but suffers a partial decomposition by the acetic acid set free in the reaction, and that the acetyl-anthranilic acid thus formed reacts with the undecomposed oxazine and the resulting carbon chain suffers condensation with the carboxyl group of the substituted anthranilic acid to give the quinoline derivative.

2-Bromo-5-furfurylideneanthranilic acid, prepared from 2-bromo-methyl-5-formylfuran and anthranilic acid, does not give the above complex reactions with acetic anhydride.

W. G.

**Interaction of Diazonium Salts and Phenols.** FREDERICK DANIEL CHATTAWAY and HENRY ROWLAND HILL (*T.*, 1922, **121**, 2756—2760).

**An Explanation of Sandmeyer's Reaction.** IVO FRANZ KEME (*Chem. Ztg.*, 1922, **46**, 1042).—The replacement of the diazo-group by chlorine, bromine, or cyanogen in the presence of the cuprous salt is explained by supposing that the cyanogen or halogen attached to the copper atom is the one which enters the benzene ring:



This view is supported by the fact that a cuprous salt which contains the group or atom which it is desired to introduce into the benzene ring must always be present.

H. C. R.

**Researches on Residual Affinity and Co-ordination. XIII. Cobaltammine and Chromic Lakes of the Azo-salicylic Acids.** GILBERT T. MORGAN and J. D. MAIN SMITH (*T.*, 1922, **121**, 2866—2874).

**Vat Dyes of the Azo-series.** DHIRENDRA NATH MUKERJI (*T.*, 1922, **121**, 2879—2882).

**Certain Triphenylmethane Dyes.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 2626—2628).—Certain dyes of the malachite-green series have been pre-

pared with a view to study their bactericidal action. The dyes were prepared in the usual way by the oxidation of the leuco-compounds with lead peroxide, and the leuco-compounds were prepared either from the corresponding aldehyde and dialkylaniline or from benzhydrol and the substituted aniline. In a number of cases where the chloride and sulphate proved too soluble for convenient manipulation, the nitrate, being less soluble, was prepared. Malachite-green and brilliant-green may be readily isolated and purified in this form. The following derivatives of leucomalachite-green are described: *m*-Acetylamido-, m. p. 154·5–155·5°; *m*-carb-amido-, m. p. 194–196°; *p*-diethylamino-, m. p. 142–144·5°; *o*-chloro-*p*-dimethylamino-, m. p. 170–171·5°; 2-hydroxy-5-benzene-azo-, m. p. 186–187°, and 2-hydroxy-5-*p*-methoxybenzeneazo-, m. p. 187–188°. The derivatives of malachite-green in the form of the following salts were prepared: *p*-Methyl- as its chloride, m. p. 160°; *o*-chloro- as its chloride, m. p. 170°; *p*-chloro- as its nitrate, m. p. 120–175°; *p*-nitro- as its chloride, m. p. 150–155°; *p*-acetyl-methylamido- as its nitrate, m. p. 193–196°; *o*-chloro-*p*-dimethyl-amino- as its chloride, m. p. 185–190°; *m*-carb-amido- as its nitrate, m. p. 185°; *o*-hydroxy- as its chloride, m. p. 195°; *p*-hydroxy- as its chloride, m. p. 185–190°; *o*-methoxy- as its nitrate; *m*-methoxy- as its carbinol, m. p. 147–149·5°; *p*-methoxy- as its chloride, m. p. 125–140°; *o*-ethoxy- as its carbinol, m. p. 178–180°; *p*-ethoxy- as its chloride, m. p. 150°; 3:4-methylenedioxy- as its chloride, m. p. 155–160°; the anhydride from the *o*-hydroxy-acetic acid, m. p. 170–175°; furyl- as its nitrate, m. p. 190°. The m. p. of the salts as given above are also decomposition points.

W. G.

**The Diazo-reaction in the Carbazole Series.** Carbazole-3-diazoimine and -3-diazonium Salts. GILBERT T. MORGAN and HUGH NORMAN READ (T., 1922, 121, 2709–2717).

**Electrolytic Preparation of Phenylhydrazine.** HIDEO WACHI (Japan Pat. 40194).—Pure phenylhydrazine can be prepared from sodium diazobenzenesulphonate by electrolytic reduction in the presence of sodium hydrogen sulphite. Aniline 25 g., and sodium carbonate 20 g., are dissolved in water 300 g., and sulphur dioxide is passed into the liquid until the solution becomes clear. It is then added, drop by drop, to the calculated quantity of sodium nitrite previously neutralised with acetic acid, to which 30 c.c. of saturated sodium hydrogen sulphite solution has been added. The solution is electrolysed, using spongy zinc or tin rods as electrodes, the operation being conducted at 30–35° during three hours, using a current of 7 volts and a current density 5 amperes per sq. dm. On concentrating the solution and then adding hydrochloric acid to it, phenylhydrazine hydrochloride separates.

K. K.

**Action of Ultra-violet Light on Egg-albumin in Relation to the Isoelectric Point.** JANET H. CLARK (*Amer. J. Hyg.*, 92, 2, 322–324; cf. *Amer. J. Physiol.*, 1922, 61, 72).—With solutions of egg-albumin of  $P_H > 4.8$ , ultra-violet light causes

aggregation and flocculation; otherwise an increase in dispersion results. Changes in charge are accompanied by change in chemical properties. As the  $p_H$  becomes less than 4.8, the precipitation on half-saturation with ammonium sulphate increases. Positively, but not negatively, charged particles of albumin are precipitated by sulphate-ions.

CHEMICAL ABSTRACTS.

**The Reduction of Methæmoglobin by Ammonium Sulphide.**

G. QUAGLIARIELLO (*Arch. di Scien. Biol.*, 1922, 3, 308—312; from *Physiol. Abstr.*, 1922, 7, 400).—Ammonium sulphide reduces methæmoglobin slowly in the cold, rapidly on warming, but without the formation of intermediate products. Oxyhæmoglobin is formed after reduction has taken place if the solution is shaken.

W. O. K.

**Hæmocyanin. III. The Absorption of Light by Oxyhæmocyanin.**

G. QUAGLIARIELLO (*Publ. St. Zool. Napoli. Ric. fisiol. chim. biol.*, 1922, 1, 57; from *Physiol. Abstr.*, 1922, 7, 405—406; cf. A., 1921, i, 467).—Oxyhæmocyanin from molluscs and arthropods shows one band in the yellow and the beginning of another in the blue. The former band is due to the copper contained in an atomic form in oxyhæmocyanin, and corresponds with  $\lambda$  579  $\mu\mu$  in molluscs and  $\lambda$  563  $\mu\mu$  in arthropods. The second band corresponds with  $\lambda$  475  $\mu\mu$  in both types, and with the second band observed by Dhéré in the ultra-violet. Reduced hæmocyanin does not show any absorption band. Oxyhæmocyanin does not form with potassium ferricyanide any compound analogous to methæmoglobin.

W. O. K.

**The Classification of the Nucleic Acids and the Place of Guanylnucleic Acid in the System.**

R. FEULGEN (*Z. physiol. Chem.*, 1922, 123, 197—204).—A general review of the nucleic acids and of their nomenclature and classification.

W. O. K.

**Guanylnucleic Acid.** R. FEULGEN (*Z. physiol. Chem.*, 1922, 123, 145—158).—In the guanylnucleic acid described by the author (A., 1921, i, 76) and by Hammarsten (*ibid.*, 200), there appears to be a nucleic acid of the type of thymus-nucleic acid in organic combination. There may also be nucleotides containing a pentose.

W. O. K.

**The Isoelectric Condition of Gelatin.** SIDNEY OWEN RAWLING and WALTER CLARK (*T.*, 1922, 121, 2830—2843).

**The Two Forms of Gelatin and their Isoelectric Points.**

JOHN ARTHUR WILSON and ERWIN J. KERN (*J. Amer. Chem. Soc.*, 1922, 44, 2633—2636).—Gelatin, like collagen, shows two minimum points of swelling with change of hydrogen-ion concentration, one at  $P_H$  4.7 and the other at 7.7. These results accord with those of Loeb (A., 1918, i, 317, 318) and those of Davis and Oakes (A., 1922, i, 63) and it is suggested that the two minima represent the isoelectric points of the gel and sol forms of gelatin, respectively.

W. G.

**Keratin.** II. A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1922, **124**, 37—64; cf. A., 1922, i, 967).—The products obtained by the partial hydrolysis of keratin have been investigated with respect to precipitation by ammonium sulphate and by zinc sulphate, and the limits of precipitation of the various fractions found.  
W. O. K.

**Mechanism of the Influence of Acids and Alkalis on the Digestion of Proteins by Pepsin or Trypsin.** JOHN H. NORTHROP (*J. Gen. Physiol.*, 1922, **5**, 263—274).—The rate of digestion of various proteins by pepsin or trypsin depends on the amount of ionised protein present, being a minimum at the isoelectric point and a maximum at that hydrogen-ion concentration at which the protein is completely combined with acid or alkali to form a salt, and it does not depend on the physical properties of the protein solution.  
W. O. K.

**Invertase.** IV. R. WILLSTÄTTER and W. WASSERMANN (*Z. physiol. Chem.*, 1922, **123**, 181—196).—The invertase of autolysed yeast is much better adsorbed by aluminium or kaolin if the solution containing it is first well diluted. The same holds for precipitation by lead acetate. The facts are applied to the preparation of purified invertase.  
W. O. K.

**Additive Reactions of the Phosphorus Haloids.** V. **The Formation of an Unsaturated Phosphinic Acid.** JAMES B. CONANT and BERNARD B. COYNE (*J. Amer. Chem. Soc.*, 1922, **44**, 2530—2536; cf. A., 1920, i, 454; 1921, i, 69).—The mechanism of the formation of an unsaturated phosphinic acid previously isolated (*loc. cit.*) from acetophenone, phosphorus trichloride, and acetic acid has been established by a study of the corresponding hydroxy- and chloro-phosphinic acids. It is shown that the hydroxy-phosphinic acid which is probably first formed is very readily converted into the chloro-acid by the action of hydrochloric acid, and that the chloro-acid in turn loses hydrogen chloride, giving the unsaturated acid. When acetophenone, phosphorus trichloride, and glacial acetic acid are mixed and the mixture is saturated the next day with dry hydrogen chloride,  $\alpha$ -chloro- $\alpha$ -phenylethylphosphinic acid, m. p. 174—175°, is obtained and is readily hydrolysed by water at the room temperature to the hydroxy-acid. When heated above its melting point or more slowly when boiled in aqueous solution, the chloro-acid is converted into  $\alpha$ -phenylvinylphosphinic acid (*loc. cit.*). This unsaturated acid on bromination yields  $\alpha\beta$ -dibromo- $\alpha$ -phenylethylphosphinic acid, m. p. 186—188°, which when heated above its melting point loses hydrogen bromide, giving  $\beta$ -bromo- $\alpha$ -phenylvinylphosphinic acid, m. p. 133—135°. This acid when treated with aqueous sodium carbonate gives phenylacetylene, and in a similar manner the dibromo-acid gives  $\alpha$ -bromostyrene. By the action of water alone, the dibromo-acid is converted into  $\alpha\beta$ -dihydroxy- $\alpha$ -phenylethylphosphinic acid, m. p. 143—145°. Phenylvinylphosphinic acid when heated with hydrobromic acid in a sealed tube at 100° for seventeen hours gives

$\beta$ -bromo- $\alpha$ -phenylethylphosphinic acid. By the action of chlorine, the unsaturated acid gives  $\alpha\beta$ -dichloro- $\alpha$ -phenylethylphosphinic acid, m. p. 175–178°. W. G.

**Organic Arsenic Compounds.** [Derivatives of Phenylarsinic Acid.] A. ALBERT (U.S. Pat. 1425929, 1425930, and 1425931).—*p*-Acetylphenylarsinic acid (darkens above 340° without melting) is obtained by dissolving the hydrazone in dilute sodium carbonate solution, adding hydrazine hydrate, and after some time hydrochloric acid. The phenylhydrazone, yellow plates, decomposes above 225°. 4-Hydroxy-3-propionylphenylarsinic acid *p*-nitrophenylhydrazone, yellow needles, decomposes above 235°. The semicarbazone (?) of 3-nitro-1-hydroxyacetylphenylarsinic acid becomes brown above 240°. *p*-Aminoguanidinoacetylphenylarsinic acid decomposes above 300°. *p*-(Acetylvinyl)phenylarsinic acid semicarbazone, thick needles, becomes brown above 330°. *p*-Formylphenylarsinic acid diethylhydrazone decomposes above 140°; the phenylmethylhydrazone, feathery needles, has m. p. 295° (decomp.). Semicarbazide and 3-hydroxy-4-acetylphenylarsinic acid yield a light yellow product. Carbonylhydrazide and *p*-benzoylphenylarsinic acid yield a white, crystalline compound, almost unchanged at 360°. Similar compounds are obtained from malonylhydrazide and oxalylhydrazide.

Treatment with sodium hyposulphite, phosphorous acid, phosphorus trichloride, hydrogen iodide, sulphur dioxide, or sodium hydrogen sulphite effects selective reduction of the arsenic yielding derivatives of trivalent arsenic, or of arsenobenzene.

#### CHEMICAL ABSTRACTS.

**The Preparation of Sulpharsphenamine.** CARL VOEGTLIN and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1922, **44**, 2573–2577).—The new compound, designated as *sulpharsphenamine*, was not obtained in the pure state. It is prepared from *arsphenamine* (1 mol.), formaldehyde (2 mols.), and sodium hydrogen sulphite (4 mols.). In its preparation, the following conditions must be observed. The solution of *arsphenamine* must be complete before the formaldehyde is added; about sixty seconds must be allowed for the formaldehyde to act before the addition of the sulphite, which should be freshly prepared from sodium carbonate and sulphur dioxide and should be added in two portions with an interval of seven minutes between the additions. The *sulpharsphenamine* is best precipitated by pouring the solution in a fine stream into five volumes of 95% alcohol and is dried by washing with absolute alcohol. It gives its free acid on decomposition with glacial acetic acid. The presence of the side chain  $\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}$  as distinct from the side chain  $\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}$  as present in *nearsphenamine* is shown by its behaviour towards the indigocarmine test of Reinking, Dehnell, and Labhardt (cf. A., 1905, i, 261). W. G.

**Examination of Nearsphenamine [Neosalvarsan].** \*II. The Constitution of the French Drugs. A. DOUGLAS MACALLUM (*J. Amer. Chem. Soc.*, 1922, **44**, 2578–2582).—Using the technique

previously described (A., 1921, ii, 420), the author has examined a number of samples of French neosalvarsan. He finds rather more variation in these samples than in American products. The most noticeable physical characteristic of the French compounds is that, unlike the neosalvarsans, which are soluble in neutral and alkaline solution alone, they dissolve unchanged in weakly acid media as well. The French compounds darken and decompose at relatively higher temperatures, are less affected by atmospheric oxygen, and are of lower toxicity and also of lower trypanocidal activity than the American preparations. Details of analyses are given.

W. G.

**An Arsenical Glucoside: Diglucosidodiaminodihydroxyarsenobenzene.** A. AUBRY and E. DORMOY (*Compt. rend.*, 1922, 175, 819—822; cf. Sokorin, A., 1888, 807; Marchlewski, A., 1894, i, 104, 511; Irvine and Moodie, T., 1908, 93, 95; Irvine and Gilmour, T., 1908, 93, 1429).—Diaminodihydroxyarsenobenzene combines with dextrose, yielding a pale yellow, crystalline powder which was shown to be diglucosidodiaminohydroxyarsenobenzene. The substance is readily soluble in water, the solution being laevorotatory,  $[\alpha]_D -560^\circ$ . When kept, it is slowly hydrolysed; after twenty days less than 40% remains unchanged. The hydrolysis may be retarded by addition of dextrose. A monoglucoside is formed as an intermediate hydrolysis product. In a discussion of the constitution, the authors point out that the glucose may be linked to the amino- or to the phenolic groups; the reactions of the substance indicate the former position.

H. J. E.

### Physiological Chemistry.

**The Comparative Concentrations of Alcohol in Human Blood and Urine at Intervals after Digestion,** WALTER R. MILES (*J. Pharm. Expt. Ther.*, 1922, 20, 265—319).—Estimations of the alcohol in the whole blood, plasma, and urine of men who had consumed a known quantity of alcohol show a greater concentration in the plasma than in the whole blood. At first, the concentrations in the blood and in the urine are approximately the same, but soon that of the urine becomes appreciably greater, and exceeds that of the plasma.

W. O. K.

**Factors which Determine the Concentration of Calcium and of Inorganic Phosphorus in the Blood-serum of Rats.** BENJ. KRAMER and JOHN HOWLAND (*Bull. Johns Hopkins Hosp.*, 1922, 33, 313—317).—The normal concentration of calcium in the serum of rats is from 9.5 to 10.5 mg. per 100 c.c. and that of phosphorus from 7 to 8.5 mg. per 100 c.c. These values were not increased by changes in the diet or by treatment with ultra-violet

light. By lowering the amount of calcium or phosphorus in the food sufficiently, the concentration of the same in the serum could be diminished by as much as 50%. Subsequent addition of fish-liver oils to the food brought the values back to normal. The same result could be obtained, with phosphorus, by illumination with light of wave-length less than 3000 Å. A similar effect could be obtained by starvation for a few days.

## CHEMICAL ABSTRACTS.

**Sodium Chloride and Selective Diffusion in Living Organisms.** JACQUES LOEB (*J. Gen. Physiol.*, 1922, 5, 231—254).—Sodium chloride, calcium chloride, and cerium chloride inhibit the diffusion of strong acids into the egg of *Fundulus* as shown by the decrease in the mortality among the eggs immersed in the acid on the addition of the chloride, and also by the decrease in the rate of fall of the hydrogen-ion concentration.  $M/8$  sodium chloride corresponds with  $M/1,000$  calcium chloride or  $M/30,000$  cerium chloride in producing this inhibition. Weak, undissociated acids are but feebly inhibited by these chlorides, if at all. The diffusion of strong alkalis is accelerated by sodium chloride, and more so by calcium chloride. Sodium chloride in moderate concentration accelerates also the diffusion of potassium chloride into the egg of *Fundulus*, whilst calcium chloride does not.

W. O. K.

**Dextrose in Eggs of Vertebrates.** G. GORI (*Atti R. accad. fisiocrit. Siena*, 1920, 21, 711—716; from *Chem. Zentr.*, 1922, iii, 927).—Dextrose is absent from the yolks of eggs of *Torpedo* and of fishes: the amount of urea present is insufficient to obscure the reaction. Using material dried first at 45° and then in a vacuum, dextrose was found to be absent from mammalian ova, present, combined and free, in birds' eggs, and present in the free state in amphibian eggs.

G. W. R.

**The Synthetic Formation of Kynurenic Acid in the Surviving Liver.** Z. MATSUOKA and S. TAKEMURA (*J. Biochem. [Japan]*, 1922, 1, 175—180).—Kynurenic acid is produced by the perfused liver of dogs when either tryptophan or indolepyruvic acid is added to the blood. It is suggested that indolepyruvic acid is probably an intermediate step in the transformation of tryptophan into kynurenic acid. This hypothesis is based on the fact that the same amount was produced (0.1285 and 0.1202 g.) with 1 g. of either the tryptophan or indolepyruvic acid in the perfusing mixture.

## CHEMICAL ABSTRACTS.

**Some Compounds Extracted from Human Skeletal Muscles.** R. ENGELAND and W. BIEHLER (*Z. physiol. Chem.*, 1922, 123, 290—294).—The following compounds have been isolated from human skeletal muscles; carnitine,  $C_7H_{15}O_3N$ ; neosine,  $C_8H_{17}O_2N$ ; myokynine,  $C_{11}H_{25}O_3N_2$ ; and mirgeline isolated as the *chloroaurate*,  $C_{11}H_{22}O_3N_2 \cdot HAuCl_4$ , light yellow, nodular crystals.

W. O. K.

**The Pharmacology of Cell Breathing. II. The Function of Iron in Cell Breathing. III. The Dependence of Cell Respiration on the Hydrogen-ion Concentration.** PH. ELLINGER and N. LANDSBERGER (*Z. physiol. Chem.*, 1922, 123, 246—263, 264—279).—Amino-acids are oxidised by oxygen in presence of an emulsion of zinc sulphide-copper phosphor in a gelatin solution, as they are in presence of charcoal (Warburg, A., 1921, i, 230; 1922, i, 190), or by an emulsion of broken-up goose erythrocytes. Potassium cyanide decreases the velocity of oxidation in the case of the goose cells, but at the same time it is itself oxidised. The rate of absorption of oxygen shows a minimum at a low concentration of potassium cyanide and the same phenomenon is observed in the case of isolated frog's muscle if potassium cyanide is applied. The oxidation is parallel to the fluorescence and phosphorescence of the cells under ultra-violet illumination. This is taken to indicate that the efficiency of the cells in catalysing oxidation is connected with the ability of the iron to lose an electron, and so activate the oxidisable material. The rate of consumption of oxygen with charcoal or with cells depends on the hydrogen-ion concentration, and this effect seems to be exerted primarily on the amino-acid which is being oxidised. W. O. K.

**The Presence of Aldol in the Urine of Diabetics.** ROBERT FRICKE (*Z. physiol. Chem.*, 1922, 124, 1—7).—Aldol in the urine of diabetics is only partly detected by the "dimedon" method previously employed (A., 1922, i, 300; ii, 326). Improvements are described which render the method more sensitive and accurate. W. O. K.

**The Sugar Content of Cerebrospinal Fluids.** K. MIFUJI (*J. Tokyo Med. Soc.*, 1921, 35, No. 10; *Japan Med. World*, 2, 78).—The normal sugar content of the spinal fluid of the Japanese averages 0.052%. The factor obtained by dividing the blood-sugar content by the spinal fluid sugar content is largest in children and least in the senile cases. In the atrophic form of beri beri the sugar content of both liquids is practically the same as normal, but in the oedematous form they are both increased. In epidemic cerebrospinal meningitis the blood-sugar content is as high as the maximum normal (0.114%) but that of the spinal fluid is remarkably decreased. In epilepsy the spinal fluid sugar content in the intermissions of an attack was low, 0.021%, but returned to normal eighteen hours after the attack. CHEMICAL ABSTRACTS.

**Pharmacology and Therapeutics of Iodides.** E. D. OSBORNE (*J. Amer. Med. Assoc.*, 1922, 79, 615—617; from *Physiol. Abstr.*, 1922, 7, 453).—After the administration of sodium iodide by the mouth, there is an increase in the concentration of sodium in the blood, whilst only a trace of iodine was found in the serum proteins when these were precipitated by tungstic acid or alcohol. On the other hand, after oral administration of potassium iodide, there is no increase of potassium in the blood, but an increase of sodium, whilst 7 to 26% of the iodine given was found in the serum proteins. W. O. K.

**Urea.** A. MARIE (*Compt. rend. Soc. Biol.*, 1922, **86**, 998; cf. *ibid.*, 1922, **86**, 72).—Intravenous injections of adrenaline hydrochloride produce a considerable increase in the urea content both of the blood and of the parenchyma of the liver freed completely from blood. Adrenaline has also been found to suppress the decomposition of urea in vitro when added to a soja bean extract. Although the vegetable urease may be entirely unlike the hepatic urease, the test-tube experiments lead to the conclusion that the increase in urea content observed after an injection of adrenaline is likewise due to a suppression of the hydrolysis of urea.

CHEMICAL ABSTRACTS.

**The Separation of Ethereal Sulphates in Rabbits after Administration of Phenol, *p*-Bromophenol, and Bromobenzene.** H. RHODE (*Z. physiol. Chem.*, 1922, **124**, 15–36).—If phenol is administered to rabbits (0.2 g. per kg.), 12% is eliminated in the urine as the ethereal sulphate, whereas if cystine, taurine, or sodium sulphite is administered at the same time, 33%, 17%, and 27%, respectively, of the phenol is eliminated. Thiosulphate and sulphate are without influence on the elimination of the phenol. In the cases of *p*-bromophenol and of bromobenzene, the effect of the simultaneous administration of cystine is to decrease the output of ethereal sulphates, the explanation apparently being that phenylmercapturic acid is formed in both cases. This indicates that the bromobenzene in the animal organism is first of all oxidised to *p*-bromophenol.

W. O. K.

**Pharmacology of Benzyl Compounds. II.** CARL NIELSEN and JOHN A. HIGGINS (*J. Lab. Clin. Med.*, 1922, **7**, 579–588; cf. *ibid.*, 1921, **6**, 388).—The observations suggest that the relaxing power of benzyl esters on the smooth muscle fibres of the intestine as a rule is dependent on the benzyl content and on the rate of hydrolysis of the benzyl compound.

CHEMICAL ABSTRACTS.

## Chemistry of Vegetable Physiology and Agriculture.

**The Relation of the Reaction and of Salt Content of the Medium to Nitrifying Bacteria.** CAROLYN S. MEEK and CHARLES B. LIPMAN (*J. Gen. Physiol.*, 1922, **5**, 195–204).—Nitrifying bacteria are particularly resistant to hydroxyl-ions, surviving in a medium of  $P_H$  13 and yielding their characteristic products in a medium of  $P_H$  11. Sodium sulphate is not nearly so toxic to these products as sodium chloride or sodium carbonate.

W. O. K.

**Nitrification. IV. The Carbon and Nitrogen Relations of the Nitrite Ferment.** AUGUSTO BONAZZI (*J. Bact.*, 1921, **6**, 479–499).—A study of the functions of autotrophic carbon assimilation and nitrogen nutrition of the nitroso-ferment. These functions are

intimately connected and mutually interdependent, the bacterial cell being able to assimilate the abundant stores of nitrogen in a nutritive solution in the absence of free carbon dioxide, even although a carbonate as such be present in the medium. Consequently the process of nitrogen oxidation which follows the absorption and leads to the formation of nitrous acid and its salts is dependent on the presence of this free carbon dioxide.

## CHEMICAL ABSTRACTS.

**Ergosterol in Yeast.** A. WINDAUS and W. GROSSKOPF (*Z. physiol. Chem.*, 1922, **124**, 8—14).—Ergosterol is extracted from yeast in a yield of about 0.15% and purified as ergosteryl acetate, m. p. 180—181°. On reduction with palladium black and hydrogen, this acetate unites with six hydrogen atoms to form *ergostanyl acetate*,  $C_{28}H_{50}O_2$ , small, white needles, m. p. 103°, which on hydrolysis yields *ergostanol*,  $C_{27}H_{48}O$ , fine leaflets, m. p. 129°. By treatment of ergostanol with phosphorus pentachloride, and subsequent reduction with sodium in amyl alcohol, the hydrocarbon, *ergostane*,  $C_{27}H_{48}$ , white leaflets, m. p. 72—73°,  $[\alpha]_D^{20} + 24.5^\circ$ , is obtained, which is not identical with sitosane,  $\psi$ -cholestane (coprostane), or cholestane. Ergostanol, on oxidation with chromic anhydride, yields *ergostanone*, fine white needles, m. p. 56—57°. W. O. K.

**Comparison of  $\alpha$ - and  $\beta$ -Glucose in Fermentation.** RICHARD WILLSTÄTTER and HARRY SOBOTKA (*Z. physiol. Chem.*, 1922, **123**, 164—169).—No difference can be detected in the rate of fermentation of  $\alpha$ - and  $\beta$ -glucose. This cannot be due to an equilibrium between the two forms being set up quickly, as the rate of this change under the conditions of the experiment is much slower than the rate of fermentation. W. O. K.

**The Selective Fermentation of Mixtures of Sugars.** RICHARD WILLSTÄTTER and HARRY SOBOTKA (*Z. physiol. Chem.*, 1922, **123**, 170—175).—Although glucose, fructose, and a mixture of these are all fermented by yeast with approximately the same velocity, yet on fermenting a mixture the glucose ferments more quickly than the fructose. This is apparently because the glucose is more active in the initial stages of fermentation whilst the final stages of the reaction are the same for both sugars. These final stages, however, are the slowest and so they decide the rate of the reaction as a whole. The same holds for the fermentation of a mixture of the  $\alpha$ - and  $\beta$ -forms of glucose (see preceding abstract). W. O. K.

**Selective Fermentation with Yeast Trained to Ferment Galactose.** RICHARD WILLSTÄTTER and HARRY SOBOTKA (*Z. physiol. Chem.*, 1922, **123**, 176—180).—Yeast may be trained so that it will ferment galactose more rapidly than glucose, but it is found that such a yeast will still preferentially ferment glucose out of a mixture of glucose and galactose. An explanation of this phenomenon is indicated on the lines suggested in the preceding abstract. W. O. K.

**The Influence of Copper Salts on the Yield of *Sterigmato-cystis nigra* [*Aspergillus niger*].** MARIN MOLLIARD (*Compt. rend.*, 1922, 175, 838—841).—The retarding action of solutions containing copper on the growth of *A. niger* renders direct comparison with the control solution of no value as the two may be at different stages of development. The author has compared the yield—i.e., the ratio of the weight of mycelium obtained to that of sugar consumed—in a control solution and one containing copper sulphate of a concentration of 1/3750, making allowance for the slower growth in the latter. The general result of the presence of copper is diminution of yield, but during a considerable portion of the time the reverse effect was observed. H. J. E.

**Some Aspects of Selective Absorption.** W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1922, 5, 225—230).—Analysis of the cell sap of the marine alga *Valonia* shows much more potassium and less sodium, magnesium, calcium, and sulphate-ion than exists in the surrounding sea-water, whilst the chloride is approximately constant. The organic material in the cell sap is small, and this seems to exclude the possibility of accounting for the high concentration of potassium by the assumption that it combines with some organic compound. W. O. K.

**Fixation and Polymerisation of Formaldehyde in the Dark by Green Plants. Carbon Dioxide Assimilation by Plants.** TH. SABALITSCHKA (*Z. angew. Chem.*, 1922, 35, 684—685).—Experiments with the nasturtium and the water-weed, *Elodea canadensis*, showed that these plants are capable of fixing formaldehyde and polymerising it to carbohydrates even in the absence of light. The plants were placed in an enclosed space and deprived of carbon dioxide. The sugar and starch content of the leaves was determined after some decrease had occurred below the normal by reason of the exclusion of carbon dioxide, and some of the plants were then exposed to formaldehyde either in the form of vapour or in solution in the case of the water weed, whilst others were kept for comparison. After some days the carbohydrates in the leaf were again estimated; as an example of the results, in one case 462 mg. of sugar and 1048 mg. of starch per 100 g. of leaf were found after treatment with formaldehyde, compared with 144 mg. of sugar and 495 mg. of starch in the blank experiment. The quantity of these substances in the formaldehyde experiment was actually higher than at the commencement, whereas in the control experiment the carbohydrates had continued to decrease. This shows that the plants were able to replenish their stock of carbohydrate, depleted by the absence of carbon dioxide, by making use of the formaldehyde, and that the polymerisation takes place in the absence of sunlight. Further, it provides additional evidence for the hypothesis that formaldehyde is an intermediate product of the photosynthesis of carbohydrates from carbon dioxide and water. G. F. M.

**Anthocyanin Pigments and Phlobatannins in Plants.** ST. JONESCO (*Compt. rend.*, 1922, 175, 904—907; cf. Combes, A., 1922, i, 206).—The red leaves of *Prunus Pissardii*, dried and powdered, were extracted with ethyl ether. The solution, on evaporation, yielded two separate substances: one, soluble in water and crystallising in tablets and needles, the other soluble in ethyl alcohol but not in water, and obtained as a yellow, amorphous substance on evaporation. Various reactions given by the former indicate that it is a tannin; the latter being precipitated by addition of water gives somewhat ambiguous results with aqueous reagents. It is, however, not converted into a red pigment when heated with dilute acids. Further extraction of the dried leaves with ethyl acetate and amyl alcohol yielded the anthocyanidins and pseudo-bases. The latter are readily transformed into anthocyanidins under the influence of dilute hydrochloric acid, their colour changing from yellow to red. The anthocyan constituents—i.e., the total of the pigments present in the various organs—are divided into anthocyanins, red, violet, or blue substances not extracted by amyl alcohol, anthocyanidins, red substances existing uncombined and readily soluble in amyl alcohol, and a third group of substances, the pseudo-bases, yellow in colour, which the author proposes to designate leuco-anthocyanidins. H. J. E.

**The Action of Hexamethylenetetramine on Higher Vegetation.** E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1922, 175, 836—838).—Solutions of hexamethylenetetramine, the concentration of which lies between 0.1 and 0.3 g. per litre, are utilised as food by beans, but on increasing the concentration a toxic effect is produced. In the former case, the action is shown by increase in weight of the plant and by the enhanced leaf development. H. J. E.

**The Chemical Constituents of Green Plants. XXII. The Presence of Succinic Acid and of Oxalic Acid in the Currant (*Ribes rubrum*).** HARTWIG FRANZEN and FRITZ HELWERT (*Z. physiol. Chem.*, 1922, 124, 65—74; cf. A., 1922, i, 310).—By converting the acids in the filtrate from the lead acetate precipitate from the currant into their esters and subsequently into the hydrazide or the benzylidene compounds, the presence of succinic acid, malic acid, and citric acid has been demonstrated. Other acids, some unsaturated, are present in traces, including probably oxalic acid, and possibly lactic acid. W. O. K.

**Colouring Matter of the Fruit of *Gardenia florida*, L.** IETSUJI MUNESADA (*J. Pharm. Soc. Japan*, 1922, No. 486, 666—671).—The colouring matter of the fruit of *Gardenia florida*, L., from China when extracted with water (cf. Kasyer, A., 1885, 59), and decomposed with dilute hydrochloric acid in a current of carbon dioxide, yielded an amorphous powder which is identical with crocetin from saffron (cf. Decker, A., 1914, i, 979). It gave a potassium salt,  $C_{10}H_{13}O_2K$ , orange-yellow crystals, sodium salt,

short, yellowish-red needles, and ammonium salt, reddish-yellow needles.

K. K.

**Preservative Principles of Hops.** I. FRANK LEE PYMAN, HAROLD ROGERSON, and THOMAS KENNEDY WALKER (*J. Inst. Brewing*, 1922, 28, 929—934).—Attempts were made to isolate crystalline hop-bitter acids by fractional extraction with alkalis of increasing strength of an ethereal solution of the soft resins, obtained by extraction of ground hops with light petroleum. Lupulon was isolated in small yield in colourless prisms, m. p. 94.5—95.5°. No humulon was obtained by this method, and the only other crystalline compounds isolated were lactic acid,  $C_{15}H_{30}O_2$ , a saturated fatty acid previously found only in the fungus *Agaricus integer*, and small quantities of the constituents of the wax, hentriacontane, ceryl alcohol, and cerotic acid.

G. F. M.

**Nitrogenous Constituents of the Fruit of Chayote (*Sechium edule*).** KIYOHISA YOSHIMURA (*J. Biochem. [Japan]*, 1922, 1, 347—351).—The fruit of *Sechium edule* (a member of the *Cucurbitaceae*) was examined with the following results: Water 95.973% and dry substance 4.027%. The dry substance contained: crude protein 16.264%, fat 1.169%, crude fibre 7.311%, nitrogen-free extract 68.392%, ash 6.864%, total nitrogen 2.602%, protein nitrogen 1.56%, and non-protein nitrogen 1.041%; that is, of the total nitrogen 59.99% was protein and 40.009% non-protein. 20 Kg. of the fresh fruit were pressed and then extracted twice with hot water; from the extract were isolated: a small quantity of adenine and choline, 0.7 g. of arginine (as nitrate), and about 1.5 g. of guanidine (as chloroaurate).

K. K.

**The Mannan of Vegetable Ivory.** II. Hemicelluloses. HANS PRINGSHEIM and KARL SEIFERT (*Z. physiol. Chem.*, 1922, 123, 205—212; cf. A., 1912, i, 833).—Mannan, prepared from vegetable ivory shavings by the action of 5% sodium hydroxide solution, is treated with acetic anhydride containing hydrogen bromide, when it yields *mannan triacetate*,  $C_8H_7O_2(OAc)_3$ , a white, amorphous, non-hygroscopic substance,  $[\alpha]_D^{25} -27.4^\circ$  in 'acetylene tetrachloride'. Mannan, on treatment with acetic anhydride containing a small amount of concentrated sulphuric acid, yields a white, amorphous substance, from which on hydrolysis and treatment with phenylhydrazine, mannosephenylhydrazone can be obtained, besides a quantity of glucosazone and also apparently the osazone of a disaccharide.

W. O. K.

**Relation of certain Nutritive Elements to the Composition of the Oat Plant.** J. G. DICKSON (*Amer. J. Botany*, 1921, 8, 256—274).—A study of the growth and composition of *Avena sativa aristata* in relation to climate and nutrition. The content of calcium oxide is reduced proportionally to its reduction in the culture solution; it is also greatly reduced by deficiency of phosphorus or nitrogen. The extent to which the content of phos-

phorus of the grain and straw is reduced by reduction in the proportion of phosphate or potassium in the culture solution, and increased by similar reduction of calcium or nitrogen, has been determined. The content of phosphorus of both grain and straw is modified by seasonal differences except for plants grown in solutions deficient in phosphorus. The content of calcium of the grain is modified even when solutions deficient in calcium are employed, whilst that of the straw shows no consistent response to climate.

CHEMICAL ABSTRACTS.

**The Comparative Assimilability of Tricalcium Phosphate and the Phosphates of Aluminium and Iron.** CH. BRIOUX (*Compt. rend.*, 1922, 175, 1096—1099).—In soils containing little or no calcium carbonate, a considerable proportion of the phosphoric acid exists as ferric or aluminium phosphate. Experiments with six different species of plants showed that, measured by the production of dried organic matter, the use of equivalent quantities of tricalcium, ferric, and aluminium phosphates results in the highest yields being obtained in the case of aluminium and the lowest with iron, although the last-named gives results considerably above the control yield. The author points out that the usual solvents for "available phosphate" give results which are inconsistent with those of his experiments, although 1% citric acid is more trustworthy than others which have been recommended.

H. J. E.

**The Availability of Mineral Plant Food (A Modification of the Present Hypothesis).** NORMAN M. COMBER (*J. Agric. Sci.*, 1922, 12, 363—369).—The conception that plants can take up from the soil only mineral matter which is in solution is criticised. Three main objections are advanced, namely, the difficulty of correlating the composition of the soil solution with the amount of mineral matter taken up by the plant; the absence of any explanation of the intake of iron by plants, and the difficulty of explaining the availability of phosphates. A modified hypothesis is presented in which the absorption of colloids by plant roots is assumed. The possibility of a definite union of root hairs with solid mineral particles is discussed, and the subsequent dissolution of the mineral particle by the organic matter of the root hair is suggested.

A. G. P.

**Theory of Soil Acidity.** J. N. MUKHERJEE (*Nature*, 1922, 110, 732).—Experimental evidence is adduced in support of the author's view (*A.*, 1922, ii, 689) concerning the origin of soil acidity. Silica has been found to adsorb appreciable quantities of acetic, citric, hydrochloric, and nitric acids so strongly that on repeated washing the adsorbed substance cannot be removed and the aqueous extract soon becomes neutral. Treatment with aqueous potassium chloride then results, however, in the development of acidity. Simultaneous experiments on electro-osmosis indicate that the anions of the acids, and not their entire molecules, are adsorbed on the surface by chemical forces, and it is suggested that an equivalent

number of kations form a mobile second sheet of the double layer, the forces acting on these being mainly electrical in nature.

A. A. E.

**Sulphur Changes in Soil.** KURT LANTZSCH (*Intern. Mitt. Bodenk.*, 1922, 12, 22—35).—Nutrient solutions containing calcium sulphate and inoculated with soil extract showed no formation of sulphide after forty-seven days. The ratio  $\text{CaO} : \text{SO}_3$  was, however, changed slightly in some cases. Nutrient solutions to which 20 g. of soil were added to 200 c.c. and allowed to remain under anaerobic conditions for sixty days showed no appreciable formation of sulphides when titrated with iodine solution. A solution containing 0.09% of potassium sulphide together with asparagine and other nutrients developed an odour of butyric acid and lost a small amount of sulphur. A somewhat similar solution containing no organic carbon showed a production of nitrogen dioxide and ammonia when ammonium chloride was the only source of nitrogen; when sodium nitrate was used instead, nitrogen dioxide and ammonia were not produced. In each case, however, some of the sulphur was oxidised to sulphate in the inoculated solutions, whilst the control gave negative results. The control tubes were treated with 0.2 c.c. of 40% formaldehyde solution per 100 c.c. of solution.

CHEMICAL ABSTRACTS.

**The Depletion of Soils by Chemical Denudation.** MILTON WHITNEY (*Science*, 1922, 56, 216—218).—The information hitherto collected concerning the rate of chemical denudation of soil and rock material has been based mainly on the translocation of material in true solution, disregarding all matter in colloidal solution. The results have shown that the loss of silica, alumina, and iron is surprisingly small in comparison with that of potassium. It is indicated, however, that in the breaking down of silicates to a point at which potassium goes into solution, silica, alumina, and iron also go into colloidal solution in the same proportion as they bear to the potassium content in the original material. This view is supported by the fact that when finely ground silicates are brought into contact with water, soluble salts go into solution (as determined by conductivity or chemical test) and at the same time there is released a relatively large amount of colloidal material. Further investigation on these lines is necessary before it will be possible to state whether chemical erosion is a selective process which might change the chemical composition of the soil, or whether, by the materials leaving the soil in about their original ratios, there is no material change in the composition of the soil on which water has acted.

A. A. E.

## Organic Chemistry.

**The Influence of the Structure of Organic Compounds on their Sulpho-chromic Oxidation.** L. J. SIMON (*Compt. rend.*, 1922, 175, 1070—1072; cf. A., 1922, ii, 867, 868).—Among the substances which are completely oxidised by the sulpho-chromic mixture are certain straight-chain compounds, phenolic derivatives, and ring-substituted aromatic acids. In other cases, molecular structure influences the extent of oxidation, e.g., methyl benzoate is completely, whilst toluic or phenylacetic acid is only partly; oxidised. From a study of a considerable number of such examples, it is seen that this method of oxidation indicates structural differences and may be used to investigate such problems as tautomerism or intramolecular change. The author has devised a formula based on the number of carbon atoms present in the molecule and the number which escape oxidation, and regards the "oxidation deficit" which it furnishes as a first step towards a new method of structural investigation.

H. J. E.

**Oxidation of Tertiary Hydrocarbons.** P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1922, 54, 351—362).—Further examples are given of the preparation of tertiary hydrocarbons by the malonic ester synthesis (cf. Levene and Cretcher, A., 1918, i, 250). The various stages of the syntheses are represented by the following series of compounds. Revised constants are given for certain compounds which have previously been described.

Ethyl ethylbutylmalonate [previously prepared, but not characterised, by Raper (T., 1907, 91, 1837)], b. p. 128—129°/7 mm.,  $d_4^{20}$  0.9646,  $n_D^{20}$  1.4284. Ethylbutylmalonic acid,  $C_8H_{16}O_4$ , m. p. 115°.  $\alpha$ -Ethylhexoic acid, b. p. 228—229° (Raper gave 225°); ethyl- $\alpha$ -ethylhexoate,  $C_{10}H_{20}O_2$ , b. p. 189—191°,  $d_4^{20}$  0.8628,  $n_D^{20}$  1.4128.  $\beta$ -Ethylhexyl alcohol,  $C_8H_{18}O$ , b. p. 181—183°,  $d_4^{20}$  0.8328,  $n_D^{20}$  1.4328;  $\beta$ -ethylhexyl iodide,  $C_8H_{17}I$ , b. p. 89—90°/11 mm.,  $d_4^{20}$  1.3365.  $\gamma$ -Methylheptane, b. p. 120—122° (cf. Clarke, A., 1909, i, 349),  $d_4^{20}$  0.7069,  $n_D^{20}$  1.3980.

Ethyl  $\alpha$ -methylheptylmalonate,  $C_{15}H_{28}O_4$ , b. p. 157—158°/10 mm.,  $d_4^{20}$  0.9496,  $n_D^{20}$  1.4324.  $\beta$ -Methylnononic acid,  $C_{10}H_{20}O_2$ , b. p. 147—148°/12 mm.,  $d_4^{20}$  0.9012,  $n_D^{20}$  1.4342; ethyl  $\beta$ -methylnononate,  $C_{12}H_{24}O_2$ , b. p. 115°/13 mm.,  $d_4^{20}$  0.8653,  $n_D^{20}$  1.4240.  $\gamma$ -Methylnonyl alcohol,  $C_{11}H_{22}O$ , b. p. 103—103.5°/9 mm.,  $d_4^{20}$  0.8342,  $n_D^{20}$  1.4361;  $\gamma$ -methylnonyl iodide,  $C_{10}H_{21}I$ , b. p. 115°/10 mm.,  $d_4^{20}$  1.2515.  $\gamma$ -Methylnonane,  $C_{10}H_{22}$ , b. p. 165.5—166.5°,  $d_4^{20}$  0.7354,  $n_D^{20}$  1.4126.

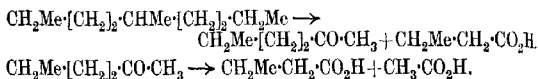
$\epsilon$ -Methylnonane ( $\beta$ -butylhexane of Levene and Cretcher, *loc. cit.*), b. p. 164—166°,  $d_4^{20}$  0.7319,  $n_D^{20}$  1.4116.

$\epsilon$ -Propylnonane,  $C_{12}H_{26}$ , b. p. 204—205°,  $d_4^{20}$  0.7559,  $n_D^{20}$  1.4228, was obtained by reduction of  $\delta$ -butyloctyl iodide (cf. Levene and Cretcher).

Ethyl butylmalonate, b. p. 122°/12 mm. (cf. Adams and Marvel, VOL. CXXIV. i.

A., 1920, i, 283),  $d_4^{20}$  0.9745,  $n_D^{20}$  1.4222. *Ethyl butylheptylmalonate*,  $C_{18}H_{34}O_4$ , b. p. 177–178°/12 mm.,  $d_4^{20}$  0.9318,  $n_D^{20}$  1.4366; *butyl heptylmalonic acid*,  $C_{14}H_{26}O_4$ , needles, m. p. 117°.  $\alpha$ -*Butylnonoic acid*,  $C_{13}H_{26}O_2$ , b. p. 179°/13 mm.,  $d_4^{20}$  0.8860,  $n_D^{20}$  1.4403; *ethyl  $\alpha$ -butylnonoate*,  $C_{15}H_{30}O_2$ , b. p. 115°/1 mm.,  $d_4^{20}$  0.8560,  $n_D^{20}$  1.4290;  $\beta$ -*Butylnonyl alcohol*,  $C_{13}H_{28}O$ , b. p. 112–114°/0.5 mm.,  $d_4^{20}$  0.8359,  $n_D^{20}$  1.4430;  $\beta$ -*butylnonyl iodide*,  $C_{13}H_{27}I$ , b. p. 121–123°/0.5 mm.  $\epsilon$ -*Methyldodecane*,  $C_{13}H_{28}$ , b. p. 225.5–227°,  $d_4^{20}$  0.7576,  $n_D^{20}$  1.4244.

When  $\epsilon$ -methylnonane was oxidised with alkaline permanganate acetic and butyric acids were identified amongst the products of the reaction; the presence of some formic acid was also detected. Apparently the oxidation proceeds mainly according to the following scheme:



E. S.

**The Formation of Hydrocarbons during the Action of Potassium on Ethyl Acetate.** HELMUTH SCHEIBLER, HEINRICH ZIEGNER, and EMIL PEPPER (*Ber.*, 1922, 55, [B], 3921–3931).—The action of potassium on an ethereal solution of ethyl acetate has been shown to lead to the formation of ethyl potassium acetate,  $\text{CH}_3\text{C}(\text{OK})\cdot\text{OEt}$  (cf. Scheibler and Voss, A., 1920, i, 366; Scheibler and Ziegner, A., 1922, i, 426). In addition, acidic substances are produced which will be described subsequently, and neutral compounds which are the subject of the present communication.

Potassium and ethyl acetate in varied proportions are allowed to react in the presence of ether and the products are decomposed either by sulphuric acid (30%) or carbon dioxide. The neutral portions are freed from admixed ester and ketones by successive treatment with concentrated potassium hydroxide solution at 80° and sodium hydrogen sulphite and are subsequently distilled, whereby a series of fractions boiling over the range 120–260° are isolated. The carbon and hydrogen content of these increases with increasing boiling point at the expense of the oxygen content. The analytical composition of the fraction b. p. 210–240°/atmospheric pressure agrees with that required by the formula  $\text{C}_{12}\text{H}_{22}$ , whereas that of the fraction b. p. above 250° harmonises with the formula  $\text{C}_{12}\text{H}_{18}$ . The constitution of the substances has not been elucidated. The insolubility of the bulk of the product in concentrated sulphuric acid indicates the absence of olefines, and the low hydrogen content makes it unlikely that paraffins are present. It is most probable that the hydrocarbons are homologues of benzene or mono- or poly-cycloparaffins.

Only traces of hydrogen are evolved in the gaseous state during the action of potassium on ethyl acetate. It appears that the liberated hydrogen reduces a portion of the ethyl potassium acetate extensively, and that in the course of the change intermediate

stances are produced which are more readily hydrogenated than ethyl potassiumacetate, a considerable proportion of which remains in the complete solution of the potassium.

The fractions boiling below  $200^{\circ}$  consist mainly of hydrocarbons, it appears to contain a certain proportion of ethers; their stability towards alkaline permanganate indicates the unsaturated nature of one or both components.

The formation of hydrocarbons is not observed when potassium is replaced by sodium under otherwise identical conditions.

H. W.

**The Chlorination of Methane.** ARTHUR SCHLEEDER and CURT JACOW (*Ber.*, 1922, 55, [B], 3710—3726).—The chlorination of methane has been studied by passing mixtures of the gases through electrically heated quartz or glass tubes. Inflammation occurs when the gases are used in molar proportions, but the flame gradually goes out; it is permanent when an excess of chlorine is employed.

On the other hand, an excess of methane is used, ignition is not observed; under these conditions chlorine is only quantitatively utilised if the temperature is not below a certain minimum depending on the precise composition and rate of flow of the mixture. The phenomena are not greatly affected by the presence of catalysts, but by an increase of temperature of  $100^{\circ}$  above the minimum. The products of the reaction are freed from hydrogen chloride by passage through warm concentrated potassium hydroxide solution. Water is unsuitable, since it dissolves appreciable amounts of methyl chloride and are subsequently condensed at a temperature not exceeding  $-110^{\circ}$ . (The vapour tensions of methyl chloride below  $-30^{\circ}$ , of methylene chloride and chloroform below  $0^{\circ}$ , and carbon tetrachloride below  $-20^{\circ}$  have been measured.) Methyl chloride can be conveniently separated from the condensate by JACOW's method of fractional distillation in a high vacuum, but the process is inapplicable to the separation of methylene chloride, chloroform, and carbon tetrachloride, which are therefore estimated approximately by the technical distillation method.

The results may be summarised as follows. When the velocity of passage of the gaseous mixture per unit of surface exceeds a certain value, and a large increase of the heating (catalysing) surface is not also provided, the reaction tends more and more towards a steady ignition, and increased formation of higher products is observed which takes place particularly at the expense of chloroform. The greater the velocity of the gas, the greater must be the catalysing surface. If the rate of flow is below the ignition value (or a suitable increase of the heating surface is provided) higher products are not formed in appreciable amount, the relative proportions of the chlorinated methanes are not those which would be expected from a step-wise reaction. When the rate of flow is below the ignition value, marked changes resulting from the production of carbon tetrachloride and higher products are observed when the catalysing surface is enormously increased (for example, by the use of activated charcoal). This result is

not appreciably modified when the minimum temperature is exceeded by as much as  $100^{\circ}$ , when the heating zone is increased or diminished, or when catalysts, such as ferric chloride, molybdenum pentachloride, or antimony pentachloride are present. On the other hand, the results obtained are not in harmony with the values calculated from Martin's formula (*Z. Elektrochem.*, 1921, 27, 150). If the rate of flow is considerably below the ignition value an increased production of chloroform and carbon tetrachloride or substances of similar boiling point at the expense of methyl and methylene chlorides is observed.

The causes which are operative in producing results differing so greatly from those of a step-wise reaction are discussed in detail. The most probable are the dissociation of methane and subsequent changes such as those represented by the equations  $\text{CH}_3\text{Cl} + \text{CH}_4 = \text{C}_2\text{H}_6 + \text{HCl}$ ,  $\text{CH}_3\text{Cl}_2 + \text{CH}_4 = \text{CH}_3\text{Cl} \cdot \text{CH}_3 + \text{HCl}$ ,  $\text{CH}_3\text{Cl} + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl} \cdot \text{CH}_3 + \text{HCl}$ , and  $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$  (or  $\text{CH}_3 \cdot \text{CHCl}_2$ ) +  $\text{HCl}$ .

The preparation of methyl chloride from methane and carbonyl chloride (cf. Hochstetter, A., 1916, i, 625) has been re-examined. The action appears to be due to greatly diluted chlorine. H. W.

**The Thallous Alkylloxides.** R. DE FORCRAND (*Compt. rend.*, 1923, 176, 20—23).—Thallous ethoxide was prepared by the method of Lamy (*Ann. Chim. Phys.*, 1863, 67, 395; 1864, 3, 373), and was isolated as an oily liquid,  $d$  3.55. It reacts with other alcohols to give the corresponding alkylloxides. In this way the author has prepared the monothallium derivatives of ethylene glycol,  $\text{OH} \cdot \text{C}_2\text{H}_4 \cdot \text{OTl}$ , and of glycerol,  $\text{C}_3\text{H}_5(\text{OH})_2 \cdot \text{OTl}$ , both of which separate as yellow solids, and thallous phenoxide, which is white and micro-crystalline. Thallous hydroxide may be similarly prepared. For the preparation of thallous acetate, the ethoxide is the best starting point, and for the neutral sulphate the hydroxide is best used.

W. G.

**The Alkylglycerols. Preparation of Alkylvinylcarbinols [Alkylallyl Alcohols].** RAYMOND DELABY (*Compt. rend.*, 1922, 175, 967—970; cf. Lespieau, A., 1911, i, 347).—Homologues of glycerol were obtained by the action of magnesium alkyl compounds on acrolein, yielding unsaturated secondary alcohols. These were brominated and the resulting bromohydrins converted into diacetins by means of potassium acetate; hydrolysis under pressure, or alcoholysis by methyl alcohol of the diacetins, then yielded the alkylglycerols. The alkylallyl alcohols obtained in the first stage have the following properties.  $\Delta^{\alpha}$ -Buten- $\gamma$ -ol (methylvinylcarbinol), b. p.  $94-96^{\circ}$ ;  $d_4^{20}$  0.854;  $d_4^{25}$  0.835;  $n_D^{20}$  1.4087 (cf. Wohl and Losanitsch, A., 1908, i, 934).  $\Delta^{\alpha}$ -Penten- $\gamma$ -ol (ethylvinylcarbinol), b. p.  $37/20$  mm.;  $d_4^{20}$  0.839;  $n_D^{20}$  1.4182 (cf. Wagner, A., 1885, 370).  $\Delta^{\alpha}$ -Hexen- $\gamma$ -ol (propylvinylcarbinol), b. p.  $133.5-134^{\circ}$ ;  $d_4^{20}$  0.851;  $d_4^{25}$  0.834;  $n_D^{20}$  1.4215.  $\Delta^{\alpha}$ -Hepten- $\gamma$ -ol (butylvinylcarbinol), b. p.  $153.5-154^{\circ}$ ;  $d_4^{20}$  0.852;  $d_4^{25}$  0.835;  $n_D^{20}$  1.4275. These alcohols yielded crystalline allophanates, m. p.  $151-152^{\circ}$ ,  $152-153^{\circ}$ ,  $139.5-140^{\circ}$ , and  $156.5-157^{\circ}$ , respectively.  $\Delta^{\alpha}$ -Hepten- $\gamma$ -ol was

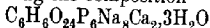
resolved into its optical isomerides by Pickard and Kenyon's method (T., 1911, 99, 45).

H. J. E.

**Alkylglycerols: Transformation of Alkylvinylcarbinols into Alkylglycerols.** RAYMOND DELABY (*Compt. rend.*, 1922, 175, 1152—1154; cf. preceding abstract).—Experimental details of the transformation of brominated alkylvinylcarbinols into diacetins and of the hydrolysis of the latter into homologues of glycerol are described. *Propylglycerol*, m. p. 60—62°, b. p. 167.5—168°/14 mm., and *butylglycerol*, m. p. 52—54°, b. p. 175—175.5°/17 mm., are hygroscopic, crystalline substances; their *triacetates* have b. p. 157—159°/15 mm., and b. p. 174°/21 mm. respectively. Methylglycerol has b. p. 162.5—163.5°/15 mm. (cf. Lieben and Zeisel, A., 1881, 710); ethylglycerol has b. p. 165—166°/15 mm. (cf. Wagner, A., 1889, 231). The method gives yields corresponding with 60% of the secondary alcohol used.

H. J. E.

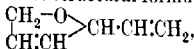
**Preparation of Inositol Polyphosphate.** SVIGEL POSTERNAK (Swiss Pat. 91727; from *Chem. Zentr.*, 1922, iv, 837—838; cf. A., 1921, i, 225).—A solution of inositol is heated with excess of orthophosphoric acid in the presence of sufficient excess of phosphoric oxide to combine with the water produced in esterification. The resulting products are dissolved in dilute sodium hydroxide solution and the sodium metaphosphate is changed into sodium pyrophosphate by heating at 100°. The latter salt is fractionally crystallised out from the viscous solution of the sodium salt of inositol polyphosphate. Other metallic inositol polyphosphates may be obtained from the sodium salt by double decomposition. Calcium, magnesium and ferric salts are mentioned and a crystalline calcium sodium salt having the composition



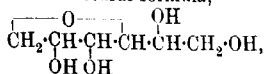
is also obtained; it probably occurs in seeds.

G. W. R.

**Cyclic Derivatives of Mannitol.** P. VAN ROMBURGH and J. H. N. VAN DER BURG (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 335—340).—The unsaturated oxide,  $\text{C}_6\text{H}_8\text{O}$ , produced by heating the hexaformate of mannitol is shown to be identical with 2-vinyldihydrofuran and its structural formula,

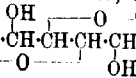


confirmed. The reduced oxide,  $\text{C}_6\text{H}_{12}\text{O}$ , prepared by reduction of  $\text{C}_6\text{H}_8\text{O}$  with hydrogen under a pressure of two atmospheres in the presence of palladium sol, is shown to be identical with 2-ethyltetrahydrofuran. The structural formula,



proposed by van Romburgh and van Maanen (*Diss. Utrecht*, 1909), for mannitan is confirmed, and that similarly proposed

for isomannide,  $\text{CH}_2-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2$ , shown probably to be



correct. *iso*Mannide increases the electrical conductivity of an aqueous solution of boric acid only very slightly. The increase in the case of mannitol and mannitan, respectively, is considerable (cf. Böseken, A., 1921, i, 843). J. S. G. T.

**Investigations on the Dependence of Rotatory Power on Chemical Constitution. XIV. The Normal Aliphatic Ethers of *d*- $\beta$ -Octanol.** JOSEPH KENYON and REGINALD ARTHUR McNICOL (T., 1923, 123, 14—22).

**The Ability of  $\alpha\gamma$ -Glycols to Form Acetone [*iso*Propylidene] Compounds.** J. BÖSEKEN and P. H. HERMANS (*Ber.*, 1922, 55, [B], 3758—3760).—Trimethylene glycol unites with acetone to form an *isopropylidene* ether, a mobile liquid with a camphoraceous odour, b. p. 123—125°,  $d_{4}^{20}$  0.9587,  $n_D^{20}$  1.4252, the isolation of which is rendered difficult by the unfavourable position of the equilibrium of the reaction, glycol + acetone  $\rightleftharpoons$  *isopropylidene* + water, and by the considerable volatility of the compound with the vapours of acetone. The relatively difficult formation of an *isopropylidene* compound from trimethylene glycol is due, not only to the presence of the hydroxyl groups in the  $\alpha\gamma$ -position and the consequent necessity of forming a six- instead of a five-membered ring, but also, and chiefly, to the unfavourable steric position of these groups. Instances in which the hydroxyl groups are more favourably placed are found in anhydroenneaheptitol (Mannich and Brose, A., 1922, i, 1118) and pentaerythritol, which yields *mono*- and *di-isopropylidene* compounds, m. p. 116° and 135°, respectively.

The place of hydrogen chloride in the condensations may be taken by other acids which are soluble in acetone. Good results are obtained with  $\frac{1}{4}$ — $\frac{1}{2}$ % of concentrated sulphuric acid, which is subsequently neutralised with a considerable excess of recently-ignited, finely-divided lime. H. W.

**Preparation of an Ester of Trichloroethyl Alcohol.** FAR BENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 358125; from *Chem. Zentr.*, 1922, iv, 888).—The alcohol is converted by the usual methods into the corresponding carbamate. For example, trichloroethyl alcohol dissolved in anhydrous ether is treated with carbamide hydrochloride, or the alcohol dissolved in benzene in the presence of quinoline is treated with carbonyl chloride, and the *trichloroethyl chloroformate* thus formed treated with ammonia. *Trichloroethyl carbamate* forms white needles, m. p. 64—65°. It is a soporific. G. W. R.

**A New Phosphoric Ester Produced by the Action of Yeast Juice on Hexoses.** ROBERT ROBISON (*Biochem. J.*, 1922, 16, 809—823).—The new ester is prepared in the following way. Lævulose or dextrose is fermented with yeast-juice and constant additions of disodium hydrogen phosphate. When the inorganic phosphate is no more utilised, barium acetate is added to the fermentation mixture, which is then neutralised and precipitated with an equal volume

of alcohol. The precipitate is then extracted with 10 parts of cold water, reprecipitated several times with basic lead acetate, purified by treatment with mercuric acetate, and finally precipitated with alcohol as the barium salt. Hexosemonophosphoric acid has  $[\alpha]_D^{25} +25.0^\circ$  in water. The metallic salts with the exception of the basic salts of the heavy metals are all readily soluble in water and are amorphous. A crystalline brucine salt was obtained. The phenylhydrazine salt of the osazone of hexosemonophosphoric acid is not identical with the isomeric compound obtained from the hexosediphosphoric acid. On hydrolysis by acids or by emulsin, the hexosemonophosphoric acid yields free phosphoric acid and a dextrorotatory substance from which glucosazone is obtained. The rotatory power of this product of degradation is, however, less than that of dextrose. S. S. Z.

**Preparation of Thiohydrins.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 185403).—Propylene thiohydrin or mixtures of this with ethylene thiohydrin are obtained by heating propylene chlorohydrin or mixtures of this with ethylene chlorohydrin such as are obtained by the action of hypochlorous acid on olefine gas mixtures, with aqueous sodium sulphide solutions, the product being isolated by evaporating the water in a vacuum, separating the sodium chloride by pressing, and distilling the crude thiohydrin under reduced pressure. *Propylene thiohydrin* boils at  $120^\circ/4$  mm., and probably has the constitution  $S(CH_2 \cdot CHMe \cdot OH)_2$ . The thiohydrins are useful as solvents in dye printing. G. F. M.

**Varying Valency of Platinum with Respect to Mercaptanic Radicles.** SIE PRAFULLA CHANDRA RAY (T., 1923, 123, 133—141).

**Stability of Sodium Formate, Acetate, and Oxalate towards Oxidation under Pressure.** HANS SCHRADER (*Ges. Abh. Kenntnis Kohle*, 1920, 5, 193—199; from *Chem. Zentr.*, 1922, iii, 1154).—At  $160^\circ$ , no oxidation of these salts takes place in three hours. Oxidation takes place freely at  $210^\circ$  and rapidly at  $260^\circ$ . Sodium formate and sodium oxalate are oxidised equally quickly, whilst sodium acetate is more slowly attacked. The presence of sodium carbonate or sodium hydroxide has no marked effect. Intermediate stages between the three organic acids and carbon dioxide were not observed. No oxalate was formed from formate, neither was oxalate or formate formed from acetate.

G. W. R.

**Investigations on the Dependence of Rotatory Power on Chemical Constitution. XIII. The Spatial Configuration of the Unbranched Aliphatic Chain.** ROBERT HOWSON PICKARD, JOSEPH KENYON, and HAROLD HUNTER (T., 1923, 123, 1—14).

**The Anodic Preparation of Pure Lead Tetra-acetate, Tetra-propionate and Silver Diacetate.** C. SCHALL and W. MELZER (*Z. Elektrochem.*, 1922, 28, 474—477).—The specific conductivities and the corresponding temperature coefficients of solutions of

anhydrous and crystalline lead diacetate in acetic acid have been measured, and the products obtained on electrolysis of these solutions examined. When the water content of the mixture is less than 0.6%, very little change is observable at the anode, and when greater than 2%, the anodic product is mainly lead dioxide. At intermediate concentrations of water, pure lead tetra-acetate may be obtained in good yield if the apparatus is surrounded by ice. The pure salt may be prepared also from a solution of the diacetate in 99.4% acetic acid in the presence of dry sodium acetate. Small amounts of lead tetrapropionate and silver diacetate may be similarly obtained. W. E. G.

**Relationship between the Iodine Values and Refractive Indices of some Hardened Vegetable Oils.** J. J. SUDBOROUGH, H. E. WATSON, and D. Y. ATHAWALE (*J. Ind. Inst. Sci.*, 1922, 5, v, 47—69).—Samples of cotton-seed, linseed, arachis, mohua (*Bassia latifolia*), sesamé, sardine, castor, hongay (*Pongamia glabra*), and coconut oils were refined and hydrogenated at 180°, using nickel catalysts, and the relationship between iodine value and refractive index was determined. Except in the case of castor and hongay oils, the relationship between the two constants is independent of the time and of the type of catalyst used. In the case of the first six oils mentioned, the curves representing the relationship between iodine value and refractive index lie very close together and may be represented by the equation  $n_D^{20} = 1.4468 + 1.03 \times 10^{-4} (I.V.) + 7.3 \times 10^{-8} (I.V.)^2$  to an accuracy of about 0.0005. The refractive indices at 60° of the above six oils, when completely hardened, are practically identical at the value 1.4468. The refractive indices of hardened coconut oil are much lower than those of other oils with the same iodine value. In the case of castor oil, the relationship between the iodine value and the refractive index is not independent of the type of catalyst or of the time of hardening owing to the varying extent to which the hydroxyl groups are reduced. It is possible that the case of hongay oil is similar, although its acetyl value is only 24. H. C. R.

**The Catalytic Decomposition of Castor Oil.** A. MAILHE (*Compt. rend.*, 1923, 176, 37—39).—When passed over aluminium and copper turnings, castor oil undergoes decomposition, the products varying with the temperature. The products are hydrocarbons and heptaldehyde. Below 600°, the hydrocarbons formed are almost entirely homologues of methane, but above 600° aromatic hydrocarbons, such as benzene, toluene, and *m*-xylene, are also formed. W. G.

**The Transition from the Colloidal to the Crystalloidal State. Solutions of Potassium Oleate.** LOUIS LEIGHTON BIRUMSHAW (*T.*, 1923, 123, 91—97).

**Dissociation Constants of Sulphoacetic and  $\alpha$ -Sulphopropionic Acids.** H. J. BACKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 359—363).—Values of the respective molecular conductivities at 25° of aqueous solutions of sulphoacetic acid,

mono- and di-sodium sulphoacetates, sulphopropionic acid, mono- and di-sodium sulphopropionates, propionanilide- $\alpha$ -sulphonic acid, and sodium propionanilide- $\alpha$ -sulphonate, in dilutions corresponding with 1 g. mol. per 16, 32, 64, 128, 256, 512, and 1024 litres have been determined. The mean values of the respective dissociation constants of sulphoacetic and  $\alpha$ -sulphopropionic acids calculated therefrom are  $8.9 \times 10^{-5}$  and  $6.0 \times 10^{-5}$  J. S. G. T.

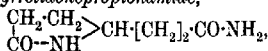
**The *cis*- and *trans*-Iridodichloro-oxalates.** Optical Resolution of the *cis*-Potassium Salt. MARCEL DELÉPINE (*Compt. rend.*, 1922, 175, 1408—1411).—Potassium iridodichloro-oxalate,  $K_2[IrCl_2(C_2O_4)_2]$ , as prepared by Vèzes and Duffour (cf. A., 1909, i, 762) was found to occur in the *cis*- and *trans*-forms, and the *cis*-form was resolved into its two optical isomerides by means of its strychnine salt. The *l*-salt is the less soluble and has  $[\alpha]_D -23.8^\circ$ . The active salts are more soluble than the racemic mixture. The *trans*-salt is not resolved by means of its strychnine salt. The *cis*- and *trans*-isomerides are capable of being transformed into one another under suitable temperature conditions. W. G.

**Investigations on the Dependence of Rotatory Power on Chemical Constitution. XVI. The Di- $\alpha$ - $\beta$ -octyl Esters of the Saturated Dicarboxylic Acids.** LESLIE HALL (T., 1923, 23, 32—44).

**The Syntheses of  $\gamma$ -Hydroxy- and  $\alpha$ -Amino- $\gamma$ -hydroxyimelic Acids.** HERMANN LEUCHS and WERNER NAGEL (*Ber.*, 1922, 55, [B], 3950—3960).—The compounds are prepared from the lactone ester,

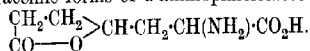
$$\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$$
 described by Leuchs and Möbis (A., 1909, i, 361). Attempts to halogenate the lactone ester, or the corresponding acid in the malonic residue and subsequently to eliminate the carbethoxy- or carboxy-group did not lead to satisfactory results, since only impure, non-crystalline products could be obtained which, even after re-esterification, could not be distilled without decomposition. The lactone ester is transformed by aniline at  $160\text{--}170^\circ$  into the *mono-anilide*,  $\text{C}_{16}\text{H}_{19}\text{O}_5\text{N}$ , lustrous leaflets, m. p.  $79\text{--}80^\circ$ . Hydrolysis of the lactone ester and subsequent removal of carbon dioxide from the product leads to the formation of the lactone of  $\gamma$ -hydroxypimelic acid,

$$\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} > \text{CH} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$$
, four- or six-sided plates, m. p.  $80\text{--}82.5^\circ$ . It is converted by methyl alcohol and hydrogen chloride into methyl  $\gamma$ -chloropimelate which could not be isolated in a homogeneous condition, but is characterised by its conversion by ammonia into  $\beta$ -pyrrolidonepropionamide,

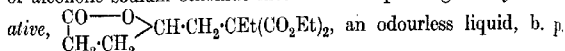


colourless needles, m. p.  $144\text{--}145^\circ$  (decomp.) when slowly heated. Hydroxypimelolactone is brominated by Volhard's method and the product is converted by methyl alcohol into the *methyl* ester

of  $\alpha$ -bromo- $\gamma$ -hydroxypimelolactone which could not be distilled without decomposition; the brominated ester is hydrolysed with boiling hydrobromic acid and the resulting acid, which could not be caused to crystallise, is aminated with aqueous ammonia. The expected products could only be isolated in the form of the copper salts, one of which ( $+H_2O$ ), sky-blue crystals, is the normal salt of  $\gamma$ -hydroxy- $\alpha$ -aminopimelic acid,  $OH\cdot CH<\begin{smallmatrix} CH_2\cdot CH(NH_2)\cdot CO_2 \\ CH_2\cdot CH_2\text{---}CO_2 \end{smallmatrix}>Cu$ , whereas the remaining two, greyish-blue crystals ( $+\frac{1}{2}H_2O$ ) and paler, greyish-blue needles ( $+\frac{1}{2}H_2O$ ), are considered to be derived from the two racemic forms of  $\alpha$ -aminopimelolactone,



The lactone ester is converted by ethyl bromide in the presence of alcoholic sodium ethoxide into the corresponding  $\alpha$ -ethyl derivative,



which is hydrolysed to a non-crystalline acid and is converted by methyl alcoholic ammonia into the *di-amide*,  $C_{10}H_{16}O_4N_2$ , colourless prisms or oblique plates, m. p.  $170\text{--}171^\circ$ . The acid is transformed by loss of carbon dioxide into  $\alpha$ -ethyl- $\gamma$ -hydroxypimelolactone, m. p.  $89\text{--}91^\circ$ , to which the constitution  $CO\text{---}O > CH\cdot [CH_2]_2\cdot CO_2H$ , is assigned. The latter substance is  $CH_2Et\cdot CH_2$

treated with bromine and a trace of phosphorus at  $100^\circ$  and the product, after being purified through the methyl ester, is treated successively with hydrobromic acid and ammonia. The product is isolated as a homogeneous copper salt,  $(C_8H_{14}O_4N)_2Cu\cdot\frac{1}{2}H_2O$ , although the constitution of the parent acid indicates the existence of four racemic isomerides; the corresponding free acid could only be obtained as a non-crystalline, very hygroscopic mass.

H. W.

**Keto-enolic Tautomerism. I. Desmotropy-isomerism of Ethyl Diacetylsuccinate.** H. P. KAUFMANN (*Annalen*, 1922, 429, 247—283).—A general account of this work has already appeared (*A.*, 1922, i, 985). The investigation shows that in 0.1N-alcoholic solution at  $30^\circ$  ethyl diacetylsuccinate becomes equilibrated to an approximation of 1 or 2% in twenty-four hours, and that the mixture then contains 10% of the  $\gamma$ -ester (diketo), 30% of the  $\beta$ -ester (diketo), 16% of the  $\alpha_2\beta$ -ester (mono-enol), and 44% of the  $\alpha_1\beta$ -ester (mono-enol). C. K. I.

**The Amphoteric Nature of the Carbonyl Group.** ERICH MÜLLER (*Z. angew. Chem.*, 1922, 35, 689—692, 698—700).—In a lecture delivered before the Dresden Chemical Society, the author gives an extended general account of his work on the electrolysis and catalytic decomposition of solutions of formaldehyde and related compounds and outlines his views on the hydration of formaldehyde to  $CH_2(OH)_2$  and the amphoteric nature of the hydrate. The observations are extended to other substances

containing the carbonyl group, such as ketones, carboxylic acids, and carbon monoxide. The assumption of the formation of ions, the existence of which cannot be demonstrated or the quantity measured, is justified by analogy with inorganic compounds such as the complex cyanides, and by the fact that the very involved behaviour of formaldehyde cannot be so clearly and uniformly explained by any other hypothesis.

H. W.

**The Photolysis of Carbonic Acid.** EMIL BAUR and A. REBER (Ann. *Helv. Chim. Acta*, 1922, 5, 828—832).—Moore and Webster are stated to have obtained formaldehyde from carbon dioxide solutions by the action of sunlight in presence of colloidal oxides of uranium or ferric iron (A., 1913, i, 1303). The present authors have repeated these experiments and have not succeeded in detecting the formation of oxalic acid, glyoxylic acid, formic acid, or formaldehyde. Failure to confirm the results obtained by the above investigators may be due to their having omitted to describe with sufficient exactitude their experimental conditions.

E. H. R.

**Acraldehyde Transformations and Antioxygenisers.**

HARLES MOUREU and CHARLES DUFRAISSE (*Bull. Soc. chim.*, 1922, [3], 31, 1152—1176; cf. Moureu and Dufraisse, A., 1919, i, 574; Moureu and Lepape, A., 1919, i, 574; 1920, i, 10; Moureu, Dufraisse, and Robin, A., 1920, i, 143; Moureu, Dufraisse, Robin, and Pougnet, A., 1920, i, 144; Moureu, Dufraisse, Lepape, Robin, Pougnet, Putaric, and Boismenu, A., 1921, i, 395; Moureu and Dufraisse, A., 1922, i, 250, 824).—A review of previous publications showing the trend of the work leading to the stabilisation of acraldehyde by addition of pyrocatechol and also by other phenols is followed by development of the subject in the direction of reviewing the chief substances capable of undergoing autoxidation and also of detecting the antioxygenising function in substances other than phenols. The oxidation of the acraldehyde appears to be a necessary preliminary to the formation of disacryl and the addition of a enol inhibits the change. But on submitting pure acraldehyde to the action of oxygen some disacryl is always formed, the quantity appearing to vary for no definite reason, although the transformation into disacryl was not observed to take place to any considerable extent in the presence of excess of oxygen. These facts appearing to be somewhat contradictory, the action of light on acraldehyde was investigated. The results showed that light effects the condensation into disacryl in absence of oxygen, and, conversely, that acraldehyde undergoes no condensation when prepared and kept in the dark and free from contact with oxygen. In absence of it, extremely small quantities of oxygen bring about the condensation, and the authors regard the phenomenon as one of catalysis, suggesting that a peroxide of acraldehyde is the catalyst. The theory put forward to account for the lack of condensation in excess of oxygen is based on the supposed existence of two species of acraldehyde molecule, one of which is activated. These molecules combine with oxygen but when oxygen is absent they

combine with each other. This is shown by the fact that acetaldehyde in contact with oxygen over mercury remains clear, the mercury meanwhile rising in the tube, but when the mercury ceases to rise oxidation is no longer occurring and the acetaldehyde becomes opaque. The time at which the latter change takes place may be predicted by extrapolating the curve obtained by plotting rise of mercury against time. Reasons are given for continued use of the term "antioxygeniser" (cf. Seyewetz and Sisley, A., 1922, ii, 628). H. J. E.

**The Hydrogenation of Aldehydes and Ketones in Presence of Pure and Impure Platinum Black.** FAULLEBIN (*Compt. rend.*, 1922, 175, 1077—1079).—In the reduction of aldehydes and ketones to alcohols in presence of platinum black, considerable experimental difficulties are experienced. The action is slow, the activity of the catalyst is in many cases extremely limited, and the yields obtained are poor owing to the formation of hydrocarbons. If, however, the catalyst is prepared by the reduction of chloroplatinic acid containing 5% of its weight of ferric chloride, good yields are obtained, especially in the case of aromatic aldehydes, and the speed of the reaction is increased. If the ferric chloride is replaced by iridium chloride, similar advantages are obtained, but to a lesser extent. In hydrogenating an ethyl acetate solution of 4-piperonyl-2-butanone in presence of "ferric platinum" to the corresponding secondary alcohol, hitherto unknown, a quantitative yield was obtained. The alcohol is not described. H. J. E.

**Syntheses by means of Sodamide.** A. HALLER (*Bull. Soc. chim.*, 1922, [iv], 31, 1073—1144).—A lecture delivered before the Société Chimique de France in which the use of sodamide as a reagent is discussed mainly with regard to the work of the author and his collaborators. The work surveyed comprises substitution reactions of ketones and nitriles, the action of the alkyl derivatives so obtained on various cyclic compounds and also the decomposition and condensation reactions which may be effected by the use of sodamide. The chief papers to which reference is made are those of von Auwers and Krollpfeiffer, A., 1915, i, 818; Bodroux and Taboury, A., 1910, i, 257; Cornubert, A., 1921, i, 730; Haller, A., 1904, i, 600; 1905, i, 214, 602; 1913, i, 629, 984, 1357; 1914, i, 418; Haller and Bauer, A., 1908, i, 987; 1909, i, 108, 654; 1910, i, 219, 300; 1911, i, 299, 726; 1913, i, 488, 829; 1914, i, 418, 549, 724; 1915, i, 411; 1918, i, 24, 428; 1922, i, 258; Haller and Benoist, A., 1912, i, 570; 1922, i, 350; Haller and Cornubert, A., 1914, i, 291, 842, 968; 1920, i, 390, 441; Haller and Louvriér, A., 1918, i, 397; Haller and Ramart-Lucas, A., 1914, i, 1072; 1917, i, 665. H. J. E.

**Diacetone-glucose [Diisopropylidene-glucose].** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1922, 54, 805—807).—When oxidised with nitric acid, the monomethyl glucose obtained from diisopropylidene-glucose yields a methyl saccharolactone,

$\gamma$ -H<sub>10</sub>O<sub>7</sub>, m. p. 206–207° (after sintering and darkening at 190°),  $[\alpha]_D^{25} +15^\circ$  (cf. Irvine and Hogg, T., 1914, 103, 1386). The production of this compound indicates that the isopropylidene radicals in diisopropylidene-glucose are attached to the  $\alpha$  and  $\epsilon$  carbon atoms. If diisopropylidene-glucose has the structure of a  $\gamma$ -glucose Irvine and Patterson, T., 1922, 121, 2146), the methyl group in the accharolactone will be attached to the  $\gamma$ -carbon atom; otherwise, it will be in the  $\beta$ -position. E. S.

**Glucosides. XI. The Glucosides of Glycerol.** P. KARRER and O. HURWITZ (*Helv. Chim. Acta*, 1922, 5, 864–869).—With the object of synthesising a glucoside of glycerol of which the constitution could not be open to doubt, the action of acetobromoglucose on isopropylidene-glycerol in presence of silver carbonate was studied. The reaction proceeded smoothly, giving a good yield of

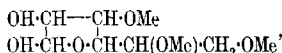
$\begin{array}{c} \text{H}_2\text{O} \\ \diagup \quad \diagdown \\ \text{H}-\text{O} \end{array} \text{CMe}_2$   $\alpha$ -tetra-acetyl-d-glucosidoglycerol iso-propylidene ether (annexed formula), white crystals, m. p. 132°,  $[\alpha]_D^{25} -20.77^\circ$ . By careful hydrolysis of this compound with dilute sulphuric acid the acetone residue was removed, leaving  $\alpha$ -tetra-acetyl-d-glucosido-glycerol, an amorphous substance which can be readily reconverted into the isopropylidene derivative. By the action of acetic anhydride on the amorphous substance the glycerol residue is acetylated, with formation of  $\alpha$ -(tetra-acetyl-d-glucosido)-glycerol  $\beta$ -diacetate, a well-crystallised compound, m. p. 98°,  $[\alpha]_D^{25} -30.96^\circ$ . Alkaline hydrolysis of the last gave 1- $\beta$ -d-glucosidoglycerol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$ ,  $[\alpha]_D^{25} -27.72^\circ$ . The  $\beta$ -configuration of the glucoside is proved by its ready hydrolysis by emulsin. It appears to be identical with the glyceryl glucoside synthesised by Bourquelot, Bridel, and Aubry by means of emulsin from glycerol and dextrose (A., 1917, i, 379). E. H. R.

**Glucosido-trimethylammonium Salts.** P. KARRER and J. ER KULE (*Helv. Chim. Acta*, 1922, 5, 870–876).—It was shown by Karrer and Smirnov (A., 1921, i, 766) that when tetra-acetyl-neosidotrimethylammonium bromide is submitted to alkaline hydrolysis, L-glucosan is formed. It is now found that by acid hydrolysis only the acetyl groups are removed, and d-glucosido- $\alpha$ -trimethylammonium bromide is formed (using hydrobromic acid for the hydrolysis) as hygroscopic crystals, m. p. 161–162°;  $[\alpha]_D^{25} +5.0^\circ$ . The hydroxide,  $\text{C}_6\text{H}_{11}\text{O}_5\cdot\text{NMe}_3\cdot\text{OH}$ , was prepared in solution by the action of silver hydroxide on the bromide or chloride; it is a strong base, but decomposes with evolution of trimethylamine when its aqueous solution is warmed. The chloride forms very hygroscopic crystals; the iodide, transparent, slightly hygroscopic crystals, m. p. 162–163°; the chloroplatinate, orange-brown crystals; chloro-pyrate, beautiful yellow needles, m. p. 141°.

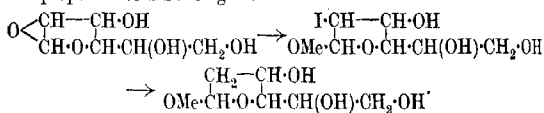
Tetra-acetyl-d-glucosido- $\alpha$ -trimethylammonium bromide forms rhombic crystals ( $a:b:c=0.4520:1:0.3443$ ); the hydroxide resembles the parent compound in preparation and properties; the chloride forms colourless hygroscopic crystals, m. p. 173°;  $[\alpha]_D^{25} +6.26^\circ$ ; the perchlorate forms microscopic needles, m. p. 190°; the picrate

crystallises in fine, yellow needles, m. p. 133°; the *chloroplatinate* in fine orange needles, m. p. 209–210° (decomp.), and the *chloroaurate* yellow needles which decompose when heated. E. H. R.

**The Constitution of Glucosan.** MARC CRAMER and EDWARD H. COX (*Helv. Chim. Acta*, 1922, 5, 884–887).—The structure proposed by Pictet and Castan (A., 1920, i, 594) for glucosan has been confirmed; the objections to this formula raised by Bergmann (A., 1921, i, 648) and Irvine and Oldham (T., 1921, 119, 1744) are therefore invalid. The attempt was first made to obtain an osazone from tribenzoylglucosan, but this was unsuccessful owing to the difficulty of hydrating the substance without hydrolysing the benzoyl groups at the same time. By the action of methyl sulphate on glucosan in presence of sodium hydroxide at 35–40°, a trimethylglucosan was obtained, b. p. 210–212°/9 mm. This gives a reducing sugar when boiled with water and forms a yellow, crystalline osazone, m. p. 163–164° (decomp.). This can only be derived from a trimethylglucose of the formula



which confirms the glucosan structure under discussion. A further proof depends on the observation that when glucosan is heated in a sealed tube with methyl iodide at 125–130° an additive compound is formed which, when reduced with sodium amalgam, gives the  $\beta$ -deoxymethylglucoside described by Fischer, Bergmann, and Schotte (A., 1920, i, 422). This reaction is readily explained by the proposed formula for glucosan thus:



E. H. R.

**Cellulose Nitrate.** EUGENE C. BINGHAM and WILLIAM L. HYDEN (*J. Franklin Inst.*, 1922, 194, 731–740).—The mobility of solutions of cellulose nitrate (12.11% nitrogen) in acetone was determined by the viscometer method at various temperatures and concentrations, and with varying shearing stresses, in order to investigate whether the fluidity is a linear function of the concentration only, or whether, as seemed probable, it is influenced by the shearing stress. It was found that there was a steady increase in the mobility with the pressure, and as already known to be the case with many plastic materials, the efflux in ml. per second was a linear function of the shearing stress. When the shearing stress is extrapolated to its value when the efflux is zero, the friction or “yield value” is obtained, which may be defined as the shearing stress at the wall of the tube necessary to start the flow. The “yield value” increased with increasing concentration and with decreasing temperature. On plotting the “yield value” against temperature for a 7.708% nitrocellulose mixture, a sharp transition temperature

was indicated at 43° where the "yield value" became zero, and the material loses its plastic character and becomes a viscous liquid. It seems probable that this transition temperature is independent of the concentration. The mobility of cellulose nitrate dispersions is characterised by the great depression produced by very small percentages of the solid, a 1% solution having a mobility only 20% of that of the pure acetone, whilst that of an 8% solution is 0.1% of that of the solvent. This is one of the most noteworthy distinctions between the polar and the non-polar type of colloid. The mobility increases with the temperature in a nearly linear manner.

G. F. M.

**Cellulose Acetate.** EMIL KNOEVENAGEL and KARL KÖNIG (*Cellulosechemie*, 1922, 3, 113—122).—Gelatinisation of solutions of cellulose acetate takes place when kept in the presence of small quantities of suitable catalysts such as sulphuric acid or sulphoacetic acid, the gelatinised product becoming insoluble in the usual solvents. If the system is not completely anhydrous, as, for instance, solutions of cellulose acetate in acetone or in glacial acetic acid, this gelatinisation may be accounted for by a large decrease in the acetyl value owing to acid hydrolysis of the ester, and it takes place more rapidly as the concentration of the catalyst is increased. If the system (solution of cellulose acetate in glacial acetic acid) be rendered anhydrous by the addition of acetic anhydride, another set of conditions arises and gelatinisation may be delayed for three months, when an increase of acetyl value and a large increase in copper value, indicative of acetolysis, are recorded. When, however, moisture is totally excluded from the first, a different type of gelatinisation is characterised, which may be described as the result of condensation or polymerisation of the cellulose ester. The purified gelatinised product is then insoluble in the usual media with the exception of tetrachloroethane, the acetyl value is only slightly changed, either slightly increased or lowered, and the copper value is slightly decreased. This type of gelatinisation may be produced by completely drying 3 g. of the cellulose acetate at 105° in a glass tube, dissolving this in 100% acetic acid sufficient to give a 15% solution, and keeping this solution in a desiccator over sulphuric acid. Next day, a small quantity of catalyst, e.g., 47 mg. of sulphuric acid or 96 mg. of sulphoacetic acid, is stirred into the viscous solution, 0.476 g. of acetic anhydride is added to react with any moisture which may have been absorbed during the operations, and the tube is sealed up. Gelatinisation takes place after two to three days, but if the quantity of catalyst is increased it is further delayed. With 115 mg. or more of sulphuric acid the solution does not gelatinise, but considerable acetolysis takes place.

J. F. B.

**Hydrocellulose [Preparation of Dimethylhydrocellulose].** EMIL HEUSER and WALTER VON NEUENSTEIN (*Cellulosechemie*, 1922, 3, 101—107).—Chopped viscose fibre, partly dried and containing 6—10% of moisture, was placed in a bottle with a paraffined

cork and the air was displaced by passing dry carbon dioxide through for two hours. A current of dry hydrogen chloride was passed very slowly so that fumes appeared at the outlet after two to three hours. The bottle was then tightly closed and allowed to remain for several hours until a test showed that the hydrocellulose was completely soluble in 10% sodium hydroxide. The fibre was neutralised and washed. For methylation, 5 g. of the hydrocellulose (1 mol.) was dissolved in 50 c.c. of 10% sodium hydroxide solution (4 mols.) and after some hours 10 g. of methyl sulphate (3 mols.) were added in small quantities at a time with continuous agitation. The temperature rose to 60° after ten minutes. Subsequent operations were performed without separating the methylated product, using the same proportions of the reagents but taking the sodium hydroxide in the form of a 25% solution instead of 10%. After the fifth operation the greater portion of the methylated cellulose remained insoluble in the saline liquid. An excess of alkali was added and while hot the cellulose ether was collected. The precipitate was dissolved in cold water, the solution filtered to remove traces of under-methylated residue, and the ether which was precipitated on heating collected while hot and washed with boiling water. When completely methylated, this ether retained its solubility in cold water even after drying. Theoretical yields were obtained when the operations were performed with mechanical stirring and the maximum degree of methylation corresponded with a methoxyl content of 33.76. (See also this vol., i, 17.)

J. F. B.

**Complex Magnesium Salts. II.** G. SPACU (*Bul. Soc. Stiinte Cluj*, 1922, 1, 247—266; from *Chem. Zentr.*, 1922, iii, 1045—1046; cf. A., 1922, i, 859).—*Magnesium tetrapyridine chloride*,  $\text{Mg}(\text{C}_5\text{NH}_5)_4\text{Cl}_2$ , prepared from magnesium chloride and anhydrous pyridine at the ordinary temperature, is a white, crystalline powder; it is very hygroscopic, with separation of pyridine. This salt differs from the corresponding bromide and iodide in that it is not co-ordinately saturated. *Magnesium triethylenediamine chloride*,  $\text{Mg en}_3\text{Cl}_2$ , forms colourless crystals which cannot be resolved into their optically active components. It is highly hygroscopic. The chloride reaction is given with silver nitrate. *Magnesium diaquodiethylenediamine iodide*,  $\text{Mg en}_2(\text{H}_2\text{O})_2\text{I}_2$ , forms crystals; it is unstable in air. *Magnesium triethylenediamine sulphate*,  $\text{Mg en}_3\text{SO}_4\text{aq}$ , is a hygroscopic, white powder. *Magnesium tetrapyridine thiocyanate*,  $\text{Mg}(\text{C}_5\text{NH}_5)_4(\text{CNS})_2$ , from magnesium thiocyanate and anhydrous pyridine, forms small, colourless, highly refractive crystals; it is very hygroscopic. *Magnesium hexapyridine thiocyanate* forms large, colourless, highly refractive crystals. *Magnesium hexammine thiocyanate*,  $\text{Mg}(\text{NH}_3)_6(\text{CNS})_2$ , prepared by the action of ammonia on solid magnesium tetrapyridine thiocyanate, is a colourless powder. Magnesium tetra-aquodipyridine chloride dipotassium chloride,  $\text{Mg}(\text{C}_5\text{NH}_5)_2(\text{H}_2\text{O})_4\text{Cl}_2 \cdot 2\text{KCl}$  is obtained by prolonged shaking of powdered carnallite with anhydrous pyridine. It is a white, crystalline powder.

G. W. R.

**Preparation of Chloro-substitution Products of Hexamethylenetetramine.** ROMOLO BURATTI (Swiss Pat. 90703; from *Chem. Zentr.*, 1922, iv, 891).—An aqueous solution of hexamethylenetetramine is mixed with a solution of a hypochlorite, previously neutralised with an organic or weak mineral acid, and the mixture concentrated to the point of crystallisation. Using neutral sodium hypochlorite containing 10% of active chlorine, the reaction is as follows:  $C_6H_{12}N_4 + 4HClO = C_6H_8N_4Cl_4 + 4H_2O$ . The tetrachlorohexamethylenetetramine thereby formed separates on concentration of the solution as a colourless mass; it forms salts with acids.

G. W. R.

**A Hydrolysis of Glycine.** EMIL BAUR (*Helv. Chim. Acta*, 1922, 5, 825—828).—When a freshly prepared solution of glycine in air-free water is shaken for a long time in absence of air with animal charcoal, gradual decomposition takes place. After 240 hours at 40°, using 10 g. of charcoal to 1 g. of glycine, 17.6% of the nitrogen present is found in solution as ammonia. Since the final solution is always neutral, the reaction is probably a simple hydrolysis according to the equation  $NH_2 \cdot CH_2 \cdot CO_2H + H_2O = OH \cdot CH_2 \cdot CO_2 \cdot NH_4$ . Attempts to separate calcium glycolate from the solution were unsuccessful, but the salt was recognised microscopically.

E. H. R.

**A Series of Metallo-cysteine Derivatives.** LESLIE JULIUS HARRIS (*Biochem. J.*, 1922, 16, 739—746).—Cysteine forms metallic derivatives much more readily than cystine. The former compound was found to give coloured metallic derivatives with the following ions:  $Fe^{+++}$ ,  $Mn^{+++}$ ,  $Mn^{+2}$ ,  $Cu^{+}$ , Co, Ni, Cr, Bi. Cuprous salts give a characteristic white derivative insoluble in neutral solutions. Tin also gives a compound with it. No oxidation takes place on addition of stannic chloride, and it is suggested that owing to the strong affinity of tin for sulphur it protects that atom in cysteine from oxidation. The mercuric ion, but not the mercurous, acts as precipitant of cysteine. The colorimetric ammonia test for cysteine is only effective in the presence of traces of a metallic compound. In alkaline solution and in the presence of oxygen, the reduced metal formed an oxygen acceptor, whilst in the absence of oxygen the oxidised metal can act as an oxygen-donor, the cysteine acting as the oxidisable substance. The system is therefore reversible so long as unoxidised cysteine is present. S. S. Z.

**The Decompositions of Mercury Fulminate.** A. LANGHANS (*Z. ges. Schiess- u. Sprengstoffw.*, 1922, 17, 122—126, 131—133, 141—143, 150—153, 159—162).—The properties of the brown product produced by drying mercury fulminate for prolonged periods (A., 1922, i, 328), and the action of dilute and concentrated nitric acid, aqua regia, sulphuric acid, chlorosulphonic acid, and hydrofluoric acid on mercury fulminate are described.

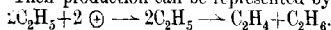
Mercury fulminate dissolves readily in boiling sodium sulphite solution. Two forms of crystals are obtained from the solution, both having the formula  $HgSO_3 \cdot Na_2SO_3 \cdot H_2O$ . If enough fulminate is added to produce a marked foaming, the salt  $Na_2SO_3 \cdot 2HgSO_3 \cdot H_2O$

is obtained. When treated with concentrated sodium sulphide solution, mercury fulminate gives off a little carbon dioxide and is coloured black owing to formation of mercuric sulphide, which dissolves in excess of the sodium sulphide. With yellow ammonium sulphide, the black precipitate at first produced turns red, and cinnabar is produced. Wet mercury fulminate is converted into mercuric sulphide, ammonium thiocyanate, and carbon dioxide by treatment with hydrogen sulphide.

Grey mercury fulminate dissolves in sodium thiosulphate, giving an almost clear solution, but the solution of white fulminate is always opalescent and a greyish-black mass is gradually deposited, which, however, shows no trace of mercury globules under the microscope. The decrease of alkalinity on keeping of a thiosulphate solution in which mercury fulminate has been dissolved is ascribed to the liberation of acid owing to the oxidising action of fulminate on the thiosulphate, the reaction being analogous to that with mercuric chloride ( $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HgCl}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{Hg}_2\text{Cl}_2 + 8 + 2\text{HCl}$ ). The change of thiosulphate into sulphate was followed quantitatively by precipitating the latter with barium chloride after various intervals of time had elapsed, and the amount of sulphate formed was found to be directly proportional to the amount of fulminate added and inversely proportional to the concentration of the thiosulphate. In using Brownson's titration method for estimating mercury fulminate, 23% of the thiosulphate was found to be converted into sulphate ten minutes after the addition of the fulminate. A thiosulphate solution stronger than  $N/10$  is recommended in this determination.

The electrolytic determination of mercury in mercury fulminate was successfully carried out, using the following solutions: potassium cyanide, ammonia, pyridine, warm 10% sodium chloride, potassium bromide, yellow sodium sulphide (10%), 2% hydrogen peroxide, 5% potassium chlorate, sodium hypochlorite, hypobromite, and hypoiodite, and ammonium oxalate. The electrolytic deposition of mercury was not quantitative using sodium thiosulphate, potassium iodide, ammonium thiocyanate, or sodium picrate. H. Ü. R.

**The Salt-like Nature of Sodium Ethyl. Indirect Electrolysis of Zinc Ethyl.** FRANZ HEIN (*Z. Electrochem.*, 1922, 28, 469—471).—A solution of sodium ethyl in zinc ethyl is a good conductor of electricity, and can be readily electrolysed, giving metallic zinc at the cathode and a mixture of hydrocarbons at the anode. The gaseous products consist of 82% of ethane and ethylene in equal proportions, and the remainder contains hydrogen and butane. Their production can be represented by the equation



These experiments prove the salt-like nature of sodium ethyl, and support the view that the solution contains  $\text{Na}^+$  and either  $\text{C}_2\text{H}_5^-$  or  $\text{Zn}(\text{C}_2\text{H}_5)_2^-$  ions. The specific conductivity of a solution of 2 mols.  $\text{NaC}_2\text{H}_5$  in 3 mols.  $\text{Zn}(\text{C}_2\text{H}_5)_2$  is 0.01082 mho at 23°. Zinc ethyl, on the other hand, does not conduct the electric current appreciably.

W. E. G.

**Is Kekulé's Benzene Theory Tenable?** C. W. A. LELY (*Chem. Weekblad*, 1922, 19, 593-598).—A triangular formula is put forward for benzene, in which the six carbon atoms, lying all in one plane, are differentiated into three primary and three secondary. The three primary form a chain of three, each having two valencies saturated by the other two primaries, and two saturated by neighbouring secondaries. The three secondaries have each two valencies saturated by primaries, and two by hydrogen atoms, the latter lying in planes perpendicular to the plane of the six carbon atoms; an additional hypothesis of synchronous rotation of the hydrogen atoms or their substituents accounts for the occurrence of only three isomeric disubstituted benzenes, and the absence of optical isomerism. Numerous reactions are cited to support the new formula, and the idea is extended to put forward formulæ for naphthalene, Willstätter's *cyclooctatetraene*, anthracene, etc.

S. I. L.

**Specimens of Cymene and Ethylbenzene of Different Origin.** K. VON AUWERS and H. KOLLIGS (*Ber.*, 1922, 55, [B], 3872-3879).—In a previous communication (*A.*, 1922, ii, 174), it has been pointed out that the physical constants of hydrocarbons of the benzene series, and in particular the refractive indices, are frequently dependent on their mode of production. Since particularly marked differences in the various specimens are noticeable in the case of cymene, the hydrocarbon has been re-examined and the observations have been extended to ethylbenzene as a simple representative of the series.

It is found that the "cymene" prepared from toluene, isopropyl bromide, and aluminium chloride is, contrary to the general rule, a meta-derivative, since it gives isophthalic acid when oxidised.

Specimens of *p*-cymene obtained from *p*- $\beta$ -iodoisopropyltoluene, cuminol, terpinene,  $\alpha$ -terpineol, and *p*- $\alpha\alpha$ -dichloroisopropyltoluene, and oil of Ajowan have closely similar physical constants if the preparation first mentioned (the uniformity of which is somewhat doubtful) is not taken into account. It is remarkable, however, that *p*-cymene derived from camphor has a particularly low refractive index; even lower values have been observed by Wheeler (Schimmel and Co., Rep., 1921, 105) for a preparation from spruce oil of turpentine.

Specimens of ethylbenzene have been examined which are obtained by reduction of freshly prepared styrene by sodium and alcohol, of acetophenone by amalgamated zinc and hydrochloric acid, by Fittig's method from bromobenzene and ethyl bromide, by Friedel and Crafts' process from thiophen-free benzene and ethyl bromide, and by the action of concentrated hydrochloric acid at 130° on *p*-ethylbenzenesulphonamide, m. p. 109°, respectively. Although all the preparations are to be regarded as "pure" in the generally accepted sense of the term, they exhibit differences in their physical constants similar to those observed with cymene. The products obtained from styrene or by Clemmensen's method have higher densities and refractive indices, whereas the constants

of all the other specimens agree well among themselves and with the values recorded previously.

Since there can be no question of steric influences in the case of ethylbenzene, it appears to be established that the differences are due to traces of impurity which cling obstinately to the various specimens. These cannot be detected by elementary analysis. Attempts to use the determination of the heat of combustion as a criterion of purity do not appear to be successful. H. W.

**Investigations on the Dependence of Rotatory Power on Chemical Constitution. XVII. A New Type of Walden Inversion.** HENRY PHILLIPS (T., 1923, 123, 44—59).

**Nitration of 3-Chloroacenaphthene.** GLADYS FARNELL (T., 1923, 123, 60—61).

**Studies in the *n*-Butyl Series. II. The Four Stereo-isomeric  $\beta$ -*Di-p*-tolylamino-*n*-butanes.** GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM (T., 1923, 123, 97—105).

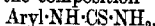
**The Reduction of Nitriles with Hydrogen in Presence of Nickel.** HANS RUPE and KARL GLENZ (*Helv. Chim. Acta*, 1922, 5, 937—942).—When optically active valeronitrile was reduced with hydrogen in presence of nickel, instead of the expected hexylamine, the secondary amine, dihexylamine, was obtained. Reduction of the nitrile with sodium and alcohol readily gave optically active hexylamine. The reaction appears to be general; since phenylacetoneitrile and  $\beta$ -phenylpropionitrile likewise gave almost entirely secondary amine when reduced with hydrogen and nickel.  $\alpha$ -Cyanocamphor did not give the corresponding secondary amine, but a base which has not been identified. When *o*-tolylearbylamine was used, it acted as a poison towards the nickel catalyst, and a poor yield of a base was obtained, probably methyl-*o*-toluidine.

The dihexylamine obtained from ordinary amyl alcohol through the cyanide had b. p. 109—115°/12 mm.; its hydrochloride,  $C_{12}H_{28}NCl$ , forms lustrous leaves; the nitrosoamine is an oil with an aromatic odour giving Liebermann's nitroso-reaction. Di- $\beta$ -phenylethylamine,  $(C_6H_5 \cdot CH_2 \cdot CH_2)_2NH$ , from phenylacetoneitrile, is a viscous oil; its hydrochloride,  $C_{16}H_{26}NCl$ , forms white, lustrous leaflets; the nitrosoamine forms white leaflets, m. p. 53—54°. Di- $\gamma$ -phenylpropylamine,  $NH(CH_2 \cdot CH_2 \cdot CH_2Ph)_2$ , gives a hydrochloride,  $C_{18}H_{24}NCl$ , white, silky leaflets; the nitrosoamine crystallises in white, felted needles, m. p. 55—56°. E. H. R.

**Phenyltrimethylammonium Perhalides.** HAMILTON MC-COMBE and THOMAS HAROLD READE (T., 1923, 123, 141—153).

**The Thiocarbimide Reaction.** SHINTARO KODAMA (*Japan. J. Chem.*, 1922, 1, 83—93).—An English version of the paper previously published in Japanese (cf. A., 1921, i, 237). K. K.

**Preparation of Complex Silver Compounds of Aromatic Thiocarbarnides.** F. HOFFMANN-LA ROCHE & Co. (Swiss Pats. 90808, 91780, and 91781; from *Chem. Zentr.*, 1922, iv, 944—945).—Aryl thiocarbarnides of the composition



the aryl group being substituted or unsubstituted, in excess are treated with silver salts such as silver chloride or silver nitrate. The complex silver compounds of the *p*-hydroxyphenylthiocarbarnide of *p*-thiocarbarnidosalicylic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\cdot(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , m. p. 221°, are thus prepared. The latter compound is prepared from 4-aminosalicylic acid hydrochloride and ammonium thiocyanate. The complex silver compound of 6-amino-3-thiocarbarnido-10-methylacridine (from 3 : 6-diamino-10-methylacridinium chloride) is also mentioned.

G. W. R.

**The Two Forms of *o*-Methylcyclohexanol.** L. MASCARELLI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 116—118).—Since the molecule of *o*-methylcyclohexanol contains two asymmetric carbon atoms having unequal rotatory values, four optically active and two racemic forms of this compound should exist. The compounds obtained by Godchot and Bédos (A., 1922, i, 334) and by Sabatier and Mailhe (A., 1905, i, 275) probably represent the two racemides. The cycloheptylcycloheptanol prepared by Godchot and Brun (A., 1922, i, 350) should exhibit similar optical isomerism to *o*-methylcyclohexanol. An analogous case is presented by the two modifications of decahydro- $\beta$ -naphthol (cf. Mascarelli, A., 1911, i, 964; Mascarelli and Recusani, A., 1912, i, 761).

T. H. P.

**The Oxide of Methyl- $\Delta^3$ -cyclohexene and the Dimethylcyclohexanols.** MARCEL GODCHOT and PIERRE BÉDOS (*Compt. rend.*, 1922, 175, 1411—1414).—It has previously been shown (A., 1922, i, 334) that the action of organomagnesium complexes on the oxide of cyclohexene gives ortho-substituted homologues of cyclohexanol and that the latter compounds are stereoisomerides of the secondary alcohols obtained by the catalytic hydrogenation of the corresponding phenols. It is now shown that, in a similar manner, methyl- $\Delta^3$ -cyclohexene gives a dimethylcyclohexanol different from those obtained by the catalytic hydrogenation of the xyenols.

*Methyl- $\Delta^3$ -cyclohexene oxide*, b. p. 141—142° (corr.),  $d^{14}_4$  0.949,  $n^{14}_D$  1.4518, is obtained from methyl- $\Delta^3$ -cyclohexene either by the action of iodine and yellow mercuric oxide followed by the action of solid potassium hydroxide on the product in ethereal solution, or by oxidation with perbenzoic acid. When heated with water at 130° for six hours it is hydrated, giving 1-methylcyclohexan-3 : 4-diol, m. p. 60°, b. p. 112—115°, which gives a diphenylurethane, m. p. 176—177°. The oxide, described above, reacts with magnesium methyl iodide to yield an alcohol, b. p. 173—174° (corr.), which is probably a 1 : 4-dimethylcyclohexan-2-ol. It has  $d^{18}_4$  0.9106,  $n^{18}_D$  1.452. It does not give a phenylurethane and on oxidation yields a dimethylcyclohexanone, b. p. 171° (corr.),  $d^{16}_4$  0.9044,  $n^{16}_D$  1.4427, which gives a semicarbazone, m. p. 122°. These physical constants are different

1:4:2-xenolol by catalytic hydrogenation and subsequent oxidation. W. G.

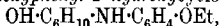
**Catalytic Hydrogenation of Liquids by means of the Common Metals. VII. Phenols.** ANDRÉ BROCHET (*Bull. Soc. chim.*, 1922, [iv], 31, 1270—1280).—The effect of temperature and pressure on the catalytic hydrogenation of phenols in presence of a reduced nickel catalyst was studied. With phenol itself, the absorption of hydrogen commences at about 50° at atmospheric pressure, and the velocity of the reaction increases rapidly as the temperature is raised to 150°. To obtain complete hydrogenation to cyclohexanol within a reasonable time, it is necessary to use pressure, however, and at 20 atmospheres and temperatures of 200—230° the absorption of 6 atoms of hydrogen per mol. was complete within an hour. For the preparation of pure cyclohexanol pressures of 10—20 atmospheres and a temperature of about 150° constitute good practical working conditions, and if an apparatus is employed in which the catalyst can be filtered from the hydrogenised product and used again with fresh phenol it is possible completely to reduce 150 g. of the latter per 1 g. of catalyst without any appreciable loss in activity. The cyclohexanol obtained boiled at 160.5°/760 mm.,  $d_4^{20}=0.950$ . The cresols are not hydrogenated appreciably below 100°, but at 150° absorption proceeds with the same facility as with phenol, and by using pressures of 10—20 atmospheres reduction to the corresponding methyl cyclohexanols was readily achieved. *o*-Methylcyclohexanol boils at 163—164°, *m*-methylcyclohexanol at 170—171°, and *p*-methylcyclohexanol at 170—171°. G. F. M.

**Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. III. Phenetidine.** JULIUS VON BRAUN and ERICH HAHN (*Ber.*, 1922, 55, [B], 3770—3779).—Under the conditions adopted by the authors, phenetidine can be hydrogenated without loss of the ethoxyl groups; the main product appears to be a mixture of stereoisomeric 4:4'-diethoxydicyclohexylamines,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_{10}\cdot\text{OEt}$ .

The hydrogenation of phenetidine is effected at 210—230° in the presence of tetrahydronaphthalene; the absorption of the gas occurs somewhat slowly, and the relative amounts of the various products appear to be considerably affected by unknown catalytic influences. About a quarter of the phenetidine used is converted into a product, b. p. 208—216°/16 mm., which can be separated by means of light petroleum into two isomeric 4-ethoxyphenyl-4'-ethoxycyclohexylamines, m. p. 78—79° and 37—38°, respectively. The isomeride of higher melting point is produced in relatively very small amount, so that it has not been possible to make a complete investigation of it. It yields a non-crystalline hydrochloride, picrate, and picrolonate, a crystalline quaternary methiodide, m. p. 156°, and an acetyl derivative, colourless crystals, m. p. 84°. The variety of lower melting point yields a non-crystalline hydrochloride, picrate, and picrolonate, an acetyl compound, m. p. 42—43°.

b. p. 235—240°/18 mm., a *nitroso*-derivative, m. p. 78°, and a very hygroscopic quaternary *methiodide* (the corresponding *methochloride* is hygroscopic, but yields a well-defined *chloroplatinate*, a micro-crystalline, orange-red powder). Fission of the quaternary ammonium hydroxide is effected very readily and gives 4-ethoxy- $\Delta^1$ -cyclohexene, a mobile liquid, b. p. 158—160° (which is converted by fuming hydrobromic acid into *trans*-1:4-dibromocyclohexane, m. p. 113°), dimethylphenetidine, m. p. 35—36° (picrate, m. p. 142°), and the tertiary base,  $C_{12}H_{27}O_2N$ , m. p. 40°, which gives a non-crystalline hydrochloride, picrate, and picrolonate.

4-Ethoxyphenyl-4'-ethoxycyclohexylamine is readily hydrolysed by concentrated hydrochloric acid at the temperature of boiling water, the ethoxyl group attached to the cyclohexyl nucleus being first affected. 4-Ethoxyphenyl-4'-hydroxycyclohexylamine,

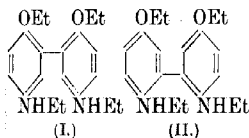


crystallises in colourless leaflets, m. p. 84—85° (*di*-p-nitrobenzoyl derivative, m. p. 192°); it loses water when distilled under diminished pressure, giving p-ethoxyphenylcyclohexenylamine,  $OEt \cdot C_6H_4 \cdot NH \cdot C_6H_9$ , a viscous, pale yellow liquid which could not be caused to solidify and has not been investigated further. 4-Hydroxyphenyl-4'-hydroxycyclohexylamine has m. p. 136—137°. 4-Ethoxyphenyl-4'-hydroxycyclohexylmethylamine,



m. p. 72°, yields a p-nitrobenzoyl compound, a pale yellow, crystalline powder, m. p. 189°.

The residues left after the distillation of 4:4'-diethoxyphenylcyclohexylamine yield a substance,  $C_{20}H_{23}O_2N_2$ , colourless crystals, m. p. 169—170°; it yields a dihydrochloride, decomp. 290°, a di-nitroso-derivative,  $C_{20}H_{26}O_4N_4$ , pale yellow crystals, m. p. 190°, and a di-acetyl compound, m. p. 240°. One of the annexed formulæ is suggested.

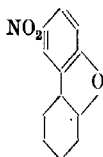


Investigations on the Dependence of Rotatory Power on Chemical Constitution. XVIII. The Di-*l*-menthyl Esters of the Saturated Dicarboxylic Acids. LESLIE HALL (T., 1923, 23, 105—113).

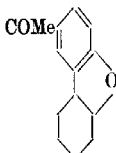
Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. II. Hexahydrodiphenylene Oxide from 1:2-Dihydroxydiphenyl. JULIUS VON BRAUN (*Ber.*, 1922, 55, [B], 3761—3770).—The catalytic reduction of 2:2'-dihydroxydiphenyl follows a somewhat unexpected course which leads to the complete hydrogenation of one nucleus and the formation of the oxide ring. The latter is extraordinarily stable towards further reduction, but readily undergoes fission when treated with oxidising agents.

Hexahydrodiphenylene oxide,  $C_6H_4 > O, C_6H_{10}$ , a colourless liquid, b. p.

138—141°/100 mm., is conveniently prepared by treating 2:2'-dihydroxydiphenyl at 230° with four atomic proportions of hydrogen and subsequent fractional distillation of the product. It is indifferent towards sodium and alcohol, zinc, and acetic acid, or magnesium phenyl bromide. It reacts slowly with bromine, but does not yield a crystalline product. Warm concentrated sulphuric acid converts it into a *monosulphonic acid*, the *sodium salt* of which is described. It is converted by cautious nitration with nitric acid (*d* 1.4) and glacial acetic acid at -15° into *nitrohexahydrodiphenylene oxide* (annexed formula), m. p. 126°, which is reduced by stannous chloride and concentrated hydrochloric acid to *aminohexahydrodiphenylene oxide*, pale yellow leaflets, m. p. 56° (*hydrochloride*, colourless needles, decomp. 250° after darkening at 225° and softening at 235°; *picrate*, m. p. 186°; *acetyl derivative*, m. p. 123°).



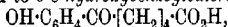
Hexahydrodiphenylene oxide readily becomes resinified under the conditions of the Friedel-Crafts' synthesis, but under definite conditions it can be converted into the corresponding *methyl ketone*



(annexed formula), colourless crystals, m. p. 67—68°. The *oxime* of the latter, m. p. 167°, is reduced by sodium and alcohol to *aminoethylhexahydrodiphenylene oxide*, a colourless liquid which rapidly absorbs atmospheric carbon dioxide, b. p. 210—213°/16 mm. (*hydrochloride*, m. p. 267—268° after darkening at 264°; *chloroplatinate*, decomp. 200° after gradual darkening; *picrate*, decomp. 250° after darkening at 240°). It is remarkable that the oxide ring is not ruptured during the reduction.

With oxalyl chloride, hexahydrodiphenylene oxide gives the acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3 > \text{O}$ , colourless crystals, m. p. 250° after softening at 240°, in very poor yield.

Hexahydrodiphenylene oxide is readily oxidised by chromic acid in glacial acetic acid to  $\delta$ -o-hydroxybenzoylvaleric acid,



long, colourless needles, m. p. 94°, b. p. 240—242°/12 mm. (*oxime*, m. p. 128°; *semicarbazone*, m. p. 186°; *phenylhydrazone*, yellow leaflets, m. p. 173°; *benzoyl derivative*, m. p. 82°). The acid is slowly converted by methyl iodide and alkali in methyl-alcoholic solution into the *methoxy-acid*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$ , m. p. 82° (*semicarbazone*, m. p. 175—176°; *methyl ester*, prismatic needles, m. p. 28°).  $\delta$ -o-Hydroxybenzoylvaleric acid is smoothly converted by isatin into 2-o-hydroxyphenyl-3-propylquinoline- $\gamma$ :4-dicarboxylic acid,  $\text{C}_6\text{H}_4 \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{C} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ , m. p. 295° (decomp.). Molten

sodium hydroxide rapidly transforms  $\delta$ -o-hydroxybenzoylvaleric acid into phenol and adipic acid.

Nitrohexahydrodiphenylene oxide is oxidised by chromic acid to  $\delta$ -m-nitro-o-hydroxybenzoylvaleric acid, small, yellow needles, m. p. 116°, which does not appear to be readily obtainable by nitration of the parent acid.

H. W.

**Elimination of the Amino-group of Tertiary Amino-alcohols. I.** ALEX. MCKENZIE and ANGUS CAMPBELL RICHARDSON (T., 1923, 123, 79—91).

**Catalytic Hydrogenation of Liquids by means of the Common Metals. VIII. Naphthols.** A. BROCHET and R. CORNUBERT (*Bull. Soc. chim.*, 1922, [iv], 31, 1280—1285).—By the hydrogenation of  $\alpha$ - and  $\beta$ -naphthols under pressure, using a reduced nickel catalyst, both the *ac*- and *ar*-tetrahydronaphthols are obtained in each case. The hydrogenation of  $\alpha$ -naphthol at 130° gives a mixture of 85% of *ac*-tetrahydro- $\alpha$ -naphthol and 15% *ar*-tetrahydro- $\alpha$ -naphthol, the former boiling at 139—140°/17 mm. (corr.) and having  $d_4^{20}$  1.0896,  $n_D^{20}$  1.5671,  $R$  44.37, showing an exaltation +0.27. It is a thick liquid, becoming brown on prolonged contact with air. The *phenylurethane* melts at 121°. *ar*-Tetrahydro- $\alpha$ -naphthol is a solid, m. p. 68° (corr.). Hydrogenation of  $\beta$ -naphthol at 150° gives 75% of the alicyclic tetrahydro-derivative, and 25% of the phenolic derivative. *ac*-Tetrahydro- $\beta$ -naphthol is a viscous liquid which darkens on contact with air and on keeping. It boils at 144.5—145.6°/20 mm. (corr.),  $d_4^{20}$  1.0715,  $n_D^{20}$  1.5523,  $R$  44.16, showing exaltation +0.06. The *phenylurethane* melts at 99°. *ar*-Tetrahydro- $\beta$ -naphthol is a solid, m. p. 57.5°. G. F. M.

**Benzo-polymethylene Compounds. II. Hydroxy-bases and  $\beta$ -Ketones of the Tetrahydronaphthalene and Hydrindene Series.** JULIUS VON BRAUN, OTTO BRAUNSDORF, and GEORG KIRSCHBAUM (*Ber.*, 1922, 55, [B], 3648—3663).—The bromine atom of *ac*-2-bromo-1-hydroxy(alkyloxy)tetrahydronaphthalenes (A., 1921, i, 407) can be replaced readily by basic residues. The hydroxy-bases formed in this manner differ greatly from *ac*- $\beta$ -aminotetrahydronaphthalene and its alkyl derivatives, since they are relatively non-toxic and have a more or less marked antipyretic character, whereas the corresponding alkyloxy-compounds are strongly poisonous. The constitution of the latter substances is established by the mode of production, but in the case of the hydroxy-compounds the possibility that the hydroxyl group may occupy position 2 is not definitely excluded (cf. Straus and Rohrbacher, A., 1921, i, 171); comparative experiments on the fission of piperidino-derivatives by cyanogen bromide indicate that this is not the case, and that the striking difference in physiological properties is therefore attributable solely to the replacement of the hydroxyl by the alkyloxy group.

The following alkyloxy-bases are described: 2-Dimethylamino-1-ethoxytetrahydronaphthalene,  $C_6H_4 \begin{smallmatrix} \text{CH(OEt)} \\ | \\ \text{CH}_2 \end{smallmatrix} \text{---} \begin{smallmatrix} \text{CH(NMe}_2) \\ | \\ \text{CH}_2 \end{smallmatrix}$ , b. p. 152°/13 mm., and its oily hydrochloride, picrate, m. p. 199°, and methiodide, m. p. 166°;  $\beta$ -piperidino-1-ethoxytetrahydronaphthalene, an almost colourless liquid, b. p. 170—172°/10 mm.; 2-diethylamino-1-alkyloxytetrahydronaphthalene, b. p. 165°/10 mm. *ac*-1-Aminotetrahydronaphthalene is readily prepared by the reduction of 1-oximinotetrahydronaphthalene with sodium and

alcohol and is converted by  $\alpha$ -dibromopentane in boiling alcoholic solution into ac-1-piperidinotetrahydronaphthalene, a colourless liquid, b. p. 174—176°/17 mm. The hydrochloride, hydrobromide, and methiodide could not be caused to crystallise; the chloroplatinate is amorphous, whereas the picrate crystallises in dark yellow needles, m. p. 145—146°, after softening at 140°. ac-2-Piperidinotetrahydronaphthalene is a colourless, odourless liquid, b. p. 186—187°/16 mm. (hydrochloride, m. p. 230—231°; hydrobromide, m. p. 233—234°; methiodide, m. p. 209°; picrate, m. p. 203—204°). Both piperidino-compounds suffer fission under the influence of cyanogen bromide, but the production of bromotetrahydronaphthalene is much more marked with the 1- than with the 2-derivative. 2-Piperidino-1-hydroxytetrahydronaphthalene (cf. Straus and Rohrbacker, *loc. cit.*) has b. p. 192—194°/14 mm., m. p. 75—76° (hydrochloride, m. p. 185—186°; picrate, m. p. 152°; chloroplatinate, m. p. 192°). 2-Piperidino-1-benzoyloxytetrahydronaphthalene is acted on by cyanogen bromide, giving cyanopiperidine in a yield which points to the presence of the basic group in the 2- rather than in the 1-position.

ac-2-Amino-1-hydroxytetrahydronaphthalene, m. p. 109°, b. p. 160°/11 mm., is prepared by the action of concentrated ammonia solution on the corresponding bromo-compound. The hydrochloride, m. p. 227°; chloroplatinate, m. p. 215°; picrate, yellow leaflets, m. p. 192°; phenylthiocarbamide, m. p. 134°; benzylidene derivative, m. p. 115°; salicylidene derivative, m. p. 108°; acetyl derivative, m. p. 203°; p-nitrobenzoyl derivative, m. p. 228°; p-aminobenzoyl derivative, m. p. 208°, and the hydrochloride of the latter, m. p. 239°, are described. When the base is warmed with an equivalent quantity of ethylene oxide in chloroform solution it is converted into 2- $\beta$ -hydroxyethylamino-1-hydroxytetrahydronaphthalene,  $C_6H_4 \begin{matrix} \text{CH(OH)·CH·NH·CH}_2\text{·CH}_2\text{·OH} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{matrix}$ , a very viscous liquid,

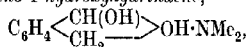
b. p. 190—196°/vacuum; the corresponding hydrochloride has m. p. 155°. 2-Benzylamino-1-hydroxytetrahydronaphthalene is a colourless, viscous liquid, b. p. 243—246°/13 mm. (picrate, m. p. 192°; hydrochloride, m. p. 237°). 2-Nortropyl-1-hydroxytetrahydronaphthalene, b. p. 210—212°/14 mm., yields a picrate, m. p. 174°, and an extremely hygroscopic hydrochloride. 2-Dimethylamino-1-hydroxytetrahydronaphthalene, m. p. 40° (cf. Straus and Rohrbacker, *loc. cit.*), yields a picrate, m. p. 138°, and a methiodide, m. p. 138—139°; the benzoate and acetate and its salts show little tendency towards crystallisation. The p-nitrobenzoate and p-aminobenzoate have m. p. 112° and 137°, respectively. 2-Methylamino-1-hydroxytetrahydronaphthalene picrate has m. p. 172°. 2-Diethylamino-1-hydroxytetrahydronaphthalene gives a crystalline chloroplatinate, m. p. 192°, and a liquid acetate.

If the methiodide of 2-dimethylamino-1-hydroxytetrahydronaphthalene is treated with silver oxide and the solution thus obtained is heated, tetrahydraironaphthalene oxide is produced. When the iodide is heated alone at a temperature very slightly above its melting point, it is decomposed into trimethylamine

hydrochloride and 2-ketotetrahydronaphthalene, b. p. 140°/20 mm., 130°/10 mm.,  $d_4^{20}$  1.1055 (*semicarbazone*, m. p. 190—191°), the yield being 80—85% of that theoretically possible. The behaviour of the ketone does not appear to be well expressed in the formula

$C_6H_4 \begin{smallmatrix} \text{CH}_2 \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{CH}_2 \end{smallmatrix}$ , which does not explain the formation of an intense blue colour under the influence of air and alkali, the difficulty with which it forms additive compounds, and the apparent absence of an activated methylene group. The application of Étard's reaction to tetrahydronaphthalene gives a mixture of the 1- and 2-ketones.

*ac*-2-Dimethylamino-1-hydroxyhydrindene,



a colourless, crystalline substance which rapidly darkens when exposed to air, b. p. 153—156°/9 mm., m. p. 62°, gives a *hydrochloride*, m. p. 183—184°, a *picrate*, m. p. 145°, and a *methiodide*, m. p. 161—162°. The latter substance is decomposed when distilled under diminished pressure into trimethylamine hydriodide and  $\beta$ -ketohydrindene; the conditions of the change are more drastic and the yield of ketone is smaller than with the corresponding tetrahydronaphthalene derivative.

H. W.

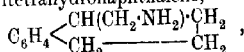
#### Benzo-polymethylene Compounds. VII. Pharmacological Analogues of *ac*-2-Aminotetrahydronaphthalene.

JULIUS VON BRAUN, HEINRICH GRUBER, and GEORG KIRSCHBAUM (*Ber.*, 1922, 55, [B], 3664—3674).—Substances which contain an aliphatic amino-group in the  $\beta$ -position with respect to an aromatic nucleus have the property of causing an increase in the blood pressure. In addition to this property, *ac*-2-aminotetrahydronaphthalene has also a mydriatic action and causes a marked increase in the body temperature. The effects obviously depend on the simultaneous presence of an aromatic and a hydroaromatic ring. The examination of a number of analogous compounds has shown that similar physiological properties are exhibited by substances which contain an aliphatic amino-group in the  $\beta$ -position to the aromatic portion of the tetrahydronaphthalene complex; if this condition is fulfilled, the further mode of attachment is immaterial.

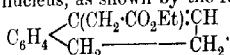
The catalytic reduction of *o*-hydroxydiphenyl with hydrogen under pressure at 210—220° in the presence of nickel salts to 2-phenylcyclohexanol is attended with considerable experimental difficulties, since the completion of the reaction is not marked by any abrupt change in the rate of absorption of the gas. The products obtained when the action is continued to the almost complete cessation of absorption are *dicyclohexyl*, b. p. 103—105°/12 mm., and 2-cyclohexylcyclohexanol, b. p. 134—135°/12 mm., which is probably a mixture of *cis*- and *trans*-isomerides (cf. Wallach, A., 1911, i, 473). The latter substance is oxidised by chromic acid to 2-cyclohexylcyclohexanone, b. p. 128—130°/10 mm. (*benzylidene* compound, m. p. 100°; *semicarbazone*, m. p.

above 200°). Less complete reduction of *o*-hydroxydiphenyl gives a mixture of phenylcyclohexane, dicyclohexyl, 2-phenylcyclohexanol, and 2-cyclohexylcyclohexanol. The alcohols are nearly exclusively produced when only six atomic proportions of hydrogen are used, but they cannot be separated conveniently from one another. Oxidation of the mixture with chromic acid gives the corresponding ketones, from which 2-phenylcyclohexanone is isolated partly in substance and partly as the *oxime*, slender needles, m. p. 174—175°; 2-phenylcyclohexanonesemicarbazone has m. p. 193°. 2-Phenylcyclohexanol, prepared by the reduction of the pure ketone with sodium and alcohol, has b. p. 143—144°/11 mm., m. p. 54—55°, and yields a phenylurethane, m. p. 138—139°. 2-Phenylcyclohexanoneoxime is reduced smoothly by sodium and alcohol to 2-phenylcyclohexylamine, b. p. 133—134°/12 mm., m. p. 59—60°. The hydrochloride, m. p. 253°, chloroplatinate, reddish-yellow needles, decomp. 222°, acetyl derivative, m. p. 130°, phenylthiocarbamide, m. p. 185°, and methiodide, m. p. 235°, are described. The base causes an increase in the blood pressure, but is not otherwise similar to *ac*-2-aminotetrahydronaphthalene, probably for the reason that the association of the aromatic and hydroaromatic nucleus is not sufficiently close.

*ac*-1-Aminomethyltetrahydronaphthalene,



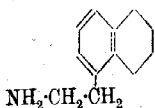
is obtained in 20% yield by the reduction of  $\alpha$ -naphthonitrile; the hydrochloride, m. p. 230°, picrate, m. p. 170°, and benzoyl derivative, m. p. 125—126°, are described. The following process does not give the base in better yield.  $\alpha$ -Ketotetrahydronaphthalene is condensed with zinc and ethyl bromoacetate to form the unsaturated ester, b. p. 183—184°/16 mm., which appears to have the double bond in the nucleus, as shown by the formula,



It is readily hydrolysed to the corresponding acid, colourless needles, m. p. 100°, which is slowly hydrogenated in the presence of palladium chloride to 1-tetrahydronaphthylacetic acid, m. p. 35—36°. The latter is convertible through the amide, but in small yield into *ac*-1-aminomethyltetrahydronaphthalene. The physiological properties of the base are similar to, but weaker than, those of *ac*-2-aminotetrahydronaphthalene.

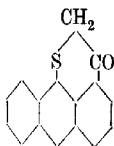
*ar*-1-Benzoylaminomethyltetrahydronaphthalene is converted by phosphorus pentachloride into *ar*-1-chloromethyltetrahydronaphthalene, b. p. 144—145°/13 mm., m. p. 50—51°. (*ar*-2-Chloromethyltetrahydronaphthalene has b. p. 141—142°/12 mm., but does not solidify when cooled.) It is converted smoothly by potassium cyanide in aqueous alcoholic solution into *ar*-1-cyanomethyltetra-

hydronaphthalene, colourless needles, m. p. 69—70°, b. p. 168—169°/10 mm. The latter is reduced by sodium and alcohol to *ar*-1- $\beta$ -aminoethyltetrahydronaphthalene (annexed formula), a colourless, somewhat viscous



liquid, b. p. 146—149°/16 mm. The corresponding *hydrochloride*, m. p. 245° (decomp.), *picrate*, small leaflets, m. p. 231°, and *benzoyl* derivative, m. p. 123°, are described. Physiologically the base closely resembles *ac*-2-aminotetrahydronaphthalene. H. W.

**The Action of Sulphur Chloride on Anthracene.** P. FRIEDLÄNDER and A. SIMON (*Ber.*, 1922, 55, [B], 3969—3980).—Anthracene is readily converted by sulphur chloride into 9-anthryl dithiochloride,  $C_{14}H_9S_2Cl$ , yellowish-red, lustrous crystals, m. p. 117—118° (decomp.), when rapidly heated; it reacts readily with ammonia and aromatic bases but only gives resinous products. With dimethylamine, it gives the compound,  $C_{14}H_9S_2NMe_2$ , yellow prisms, m. p. 70—71°; the corresponding *piperidide* is described. A solution of anthryl dithiochloride in benzene is converted by a concentrated solution of sodium sulphite at the atmospheric temperature into sodium 9-anthryl thiosulphate,  $C_{14}H_9S\cdot SO_3Na$ , pale yellow leaflets; the corresponding barium salt is intensely yellow, but appears to yield a colourless hydrate. 9-Anthryl hydrogen thiosulphate,  $C_{14}H_9S\cdot SO_3H$ , crystallises in slender, colourless needles; it decomposes slowly in warm aqueous solution, rapidly in the presence of hydrochloric acid, into sulphuric acid and 9-anthryl disulphide, lustrous, orange-yellow octahedra, m. p. 223° (see later); this compound (in addition to thiosulphate) is also produced when a solution of the sodium salt is warmed with sodium hydroxide. 9-Thiolanthracene, orange-yellow octahedra, m. p. 90—91°, is most conveniently prepared by the action of anthryl dithiochloride on a solution of hydrated sodium sulphide in methyl alcohol; the corresponding sodium salt forms orange-yellow leaflets, and the methyl ether, needles, m. p. 153°. The thiol is the sulphur analogue of anthranol (Meyer, A., 1911, i, 193), but, unlike this compound, it exhibits little tendency to pass into a substance of the anthrone type. 9-Anthryl disulphide (see above) is obtained quantitatively by the oxidation of an alkaline solution of the thiol with potassium ferricyanide. 9-Anthrylthiolacetic acid,  $C_{14}H_9S\cdot CH_2\cdot CO_2H$ , slender, very pale yellow needles, m. p. 164°, is prepared by the addition of the sodium compound of 9-thiolanthracene to an alkaline solution of sodium chloroacetate; the sodium salt, lustrous leaflets, ammonium salt, and the methyl ester, small, yellow needles, m. p. 67°, are described. The acid is converted by phosphorus pentachloride in the presence of light petroleum (but less conveniently by thionyl chloride, which also causes chlorination) into 9-anthrylthiolacetyl chloride, compact, yellow needles, from which the corresponding amide, colourless needles which soften but do not melt at 197°, is prepared. The chloride is converted by aluminium chloride in the presence of light petroleum at 30—40°, into 3-keto-peri-anthracenopenthiophen (annexed formula), small, tile-red crystals, m. p. 150—152°. The substance is transformed by hot nitrobenzene into bis-peri-anthracenopenthiophen,  $C_{14}H_9\langle\begin{smallmatrix} S \\ CO \end{smallmatrix}\rangle C:C \langle\begin{smallmatrix} S \\ CO \end{smallmatrix}\rangle C_{14}H_9$ , dark



green needles, and condenses with  $\alpha$ -isatinanilide in the presence of pyridine to give 3'-indoxyl-(2:2')-peri-anthracenopenthiophen,  

$$C_{14}H_8 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{NH} \end{array} C_6H_4$$
, dark coloured needles. H. W.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XV. Some *n*-Alkyl Ethers of *d*-Benzylmethylcarbinol. HENRY PHILLIPS (T., 1923, 123, 22—31).

The Formation and Stability of *spiro*-Compounds. X. *spiro*-Compounds Derived from *cyclo*Heptane. JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD (T., 1923, 123, 122—133).

Preparation of Esters. LABORATOIRE-USINE (F.P. 531960; from *Chem. Zentr.*, 1922, iv, 943).—Alkyl carboxylates are heated with aluminium derivatives of alcohols. The reaction takes place according to the equation,  $3R \cdot CO_2R' + Al(OR'')_3 = 3R \cdot CO_2R' + Al(OR'')_3$ , where  $R''$  has a higher molecular weight than  $R'$ . The aluminium alkyloxides are prepared by heating the corresponding alcohols with aluminium amalgam or other easily decomposed aluminium alloys. For example, aluminium amyl oxide and ethyl acetate give amyl acetate. *Amyl phenylacetate*,  $\alpha$ -*phenylethyl acetate*,  $\beta$ -*phenylethyl phenylacetate*, and *linalyl acetate* are similarly prepared. G. W. R.

Some Esters of Anisic Acid. L. G. RADCLIFFE and W. H. BRINDLEY (*Perf. Essent. Oil Rec.*, 1922, 13, 414—415).—Anisic acid was obtained in almost theoretical yield by the oxidation of anisaldehyde with alkaline permanganate. Cannizzaro's method—treatment of the aldehyde with potassium hydroxide—proved unsatisfactory, large amounts of unchanged material being recovered. The following esters were prepared by saturating solutions in the respective alcohols with dry hydrogen chloride. Methyl ester, m. p. 48°, b. p. 256°. Ethyl ester, m. p. 7—8°, b. p. 263°,  $d_4^{15}$  1.106,  $n_D^{15}$  1.5245. *n*-Propyl ester, b. p. 176°/15 mm.,  $d_4^{15}$  1.09,  $n_D^{15}$  1.5149. *n*-Butyl ester, b. p. 183°/40 mm.,  $d_4^{15}$  1.054,  $n_D^{15}$  1.5141. *iso*Butyl ester, b. p. 170°/46 mm.,  $d_4^{15}$  1.052,  $n_D^{15}$  1.5072. *iso*Amyl ester, b. p. 188°/30 mm.,  $d_4^{15}$  1.040. Phenylpropyl ester, b. p. 256°/35 mm.,  $d_4^{15}$  1.111,  $n_D^{15}$  1.5623. Only the lower members of the aliphatic series have pronounced odours, the higher members are practically odourless. G. F. M.

Preparation of Alkyl Dihydroxynaphthoylbenzoates. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 90806, 91106, and 91107; from *Chem. Zentr.*, 1922, iv, 890).—1:5- or 1:6-Dihydroxynaphthoyl-*o*-benzoic acid is esterified in the usual way with aliphatic alcohols. *Allyl* 1:6-dihydroxynaphthoyl-*o*-benzoate forms white, prismatic needles, m. p. 128°. *Ethyl* 1:6-dihydroxynaphthoyl-*o*-benzoate forms slightly yellow crystals, m. p. 156°. *Ethyl* 1:5-dihydroxynaphthoyl-*o*-benzoate forms white needles, m. p. 146°. G. W. R.

**The Degradation of Hydroaromatic Acids of the Glutaric Acid Series.** A. WINDAUS, F. KLÄNHARDT, and G. REVEREY (*Ber.*, 1922, 55, [B], 3981—3987).—In a previous communication (Windaus and Klänhardt, A., 1921, i, 392), it has been shown that the silver salts of the aliphatic glutaric acids react with iodine in accordance with the schemes  $\text{CO}_2\text{Ag}[\text{CH}_2]_3\text{CO}_2\text{Ag} + \text{I}_2 = 2\text{AgI} + -\text{O}-\text{CO}[\text{CH}_2]_3\text{CO}-\text{O}-$  and  $-\text{O}-\text{CO}[\text{CH}_2]_3\text{CO}-\text{O}- \rightarrow$  (a)  $\text{CO}[\text{CH}_2]_3\text{CO} + \text{O}$ , or (b)  $\text{CO}[\text{CH}_2]_2\text{CH}_2 + \text{CO}_2$ , or (c)  $\text{CH}_2\text{:CHMe} +$

$2\text{CO}_2$ . The observations have now been extended to acids which may be regarded as glutaric acids of which one or more carbon atoms are members of a hydroaromatic ring. The action is found to occur normally in the case of the *cis*-acids unless the glutaric acid substitutes a five-membered ring in the 1:3-position.

Silver *cyclohexanediacetate* is converted by iodine into the

lactone,  $\text{CH}_2\langle\text{CH}_2\text{CH}_2\rangle\text{C}\langle\text{CH}_2\text{O}\text{CH}_2\text{CO}\rangle$ , a colourless, viscous liquid,

b. p. 273°/759 mm. (slight decomp.), 154°/16 mm.,  $d_{15}^{20}$  1.0755,  $n_D^{20}$  1.48386,  $n_D^{20}$  1.48668,  $n_D^{20}$  1.48631. The *barium* and *potassium* salts

of the corresponding hydroxy-acid have been prepared. The lactone is oxidised by alkaline permanganate or by potassium dichromate and sulphuric acid to *cyclohexane-1-acetic-1-carboxylic*

acid,  $\text{CH}_2\langle\text{CH}_2\text{CH}_2\rangle\text{C}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , colourless prisms, m. p. 131° (uncorr.) [cf. Norris and Thorpe, T., 1921, 119, 1206].

Silver *cis*-hexahydrohomophthalate is readily converted by

iodine into *hexahydrophthalide*,  $\text{CH}_2\text{CH}_2\langle\text{CH}\text{CH}_2\rangle\text{O}$ , a colourless

liquid, b. p. 134—138°/25 mm., the constitution of which is established by its oxidation with potassium dichromate and sulphuric acid to *cis*-hexahydrophthalic acid; the same lactone is obtained in smaller yield and with greater difficulty from silver *trans*-hexahydrohomophthalate.

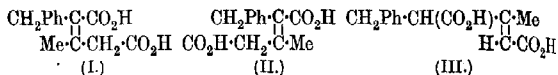
*iso*Phthalic acid is hydrogenated in glacial acetic acid solution to a mixture of *cis*- and *trans*-hexahydro*iso*phthalic acids, in which the former preponderates the more considerably when the reduction proceeds rapidly; the *cis*-acid, however, is not converted into the *trans*-variety if subsequently agitated with glacial acetic acid and platinum black. Silver *cis*-hexahydro*iso*phthalate and iodine give the lactone of *cis*-cyclohexanol-3-carboxylic acid, b. p. 127—135°/21 mm. (cf. Perkin and Tattersall, T., 1907, 91, 488) the identity of which is established by converting it into *cis*-cyclohexanol-3-carboxylic acid, m. p. 132—133°, and *cis*-3-bromocyclohexanecarboxylic acid, m. p. 61—63°.

Silver camphorate is transformed by iodine into camphoric anhydride; a neutral lactone does not appear to be produced.

H. W.

**The Chemistry of the Glutaconic Acids. XIII. The Isomerism due to Retarded Mobility.** JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD (T., 1923, 123, 62—64).

**$\alpha$ -Benzyl- $\beta$ -methylglutaconic Acids.** FRANZ FEIST and E. D. RAUTERBERG (*Ber.*, 1922, 55, [B], 3697—3705).—In extension of previous investigations (A., 1922, i, 521, 522, 553), the authors have examined the ozonisation of a substituted glutaconic acid which might be expected to yield stable fission products, and for this purpose have selected  $\alpha$ -benzyl- $\beta$ -methylglutaconic acid (cf. Bland and Thorpe, T., 1912, 101, 1740). It is shown that the (normal) acid of higher melting point and its esters and also the esters of the labile acid are constituted in accordance with the annexed formula (I), whereas the labile acid appears to be a mixture of the two *trans*-forms (II and III). The complex nature of the



latter product explains its low melting point as compared with that of the homogeneous *cis*-acid.

*cis*- $\alpha$ -Benzyl- $\beta$ -methylglutaconic acid gives an *ozonide* which is hydrolysed to phenylpyruvic acid, m. p. 153—154° [oxime, m. p. 159°, *phenylhydrazone*, m. p. 187—188° (decomp.)], acetone, and carbon dioxide. The *ozonide* of its ethyl ester similarly yields ethyl benzylglyoxylate and ethyl acetoacetate. *trans*- $\alpha$ -Benzyl- $\beta$ -methylglutaconic acid is converted successively into its *ozonide* and acetic acid, phenylethyl methyl ketone, and benzoic acid; the formation of oxalic and glyoxylic acids could not be established. The *ozonide* of ethyl *trans*- $\alpha$ -benzyl- $\beta$ -methylglutaconate is hydrolysed to acetic acid, ethyl acetoacetate, (?) ethyl phenylpyruvate, and benzoic acid.

Ethyl phenylpyruvate is converted into a *diphenylhydrazone*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{N}\cdot\text{NPh}_2)\cdot\text{CO}_2\text{Et}$ , small, yellow crystals, m. p. 105°, and a *p*-nitrophenylhydrazone, pale yellow crystals, m. p. 181°. H. W.

**Ring-chain Tautomerism. IV. The Effect of the Methyl Ethyl Grouping on the Carbon Tetrahedral Angle.** BALBIR SINGH and JOCELYN FIELD THORPE (T., 1923, 123, 113—122).

**Composition of Erythrosin.** M. GOMBERG and D. L. TABERN (*J. Ind. Eng. Chem.*, 1922, 14, 1115—1117).—Pure tetraiodofluorescein was prepared by direct halogenation of fluorescein in hot dilute acetic acid with excess of iodine, and subsequent purification by washing with dilute sulphuric acid and alcohol and precipitation from solution in dilute sodium hydroxide. This product did not contain free iodine but was amorphous, and the iodine content was low owing to the presence of about 6% of diiodofluorescein, from which it was purified by conversion, by boiling with acetic anhydride, into the diacetate which, after three recrystallisations from bromobenzene alternated with acetone, was obtained analytically pure and melting at 293—294°. Hydrolysis of the acetate gave pure crystalline tetraiodofluorescein. This was converted into erythrosin by neutralisation with sodium carbonate in suspension in absolute alcohol. The salt was deposited in red

crystals after concentration of the solution and addition of ether. It contained both water and alcohol of crystallisation, and the former was not completely expelled even by long drying at 160—170°. The fully hydrated salt contains  $4\text{H}_2\text{O}$ , and the conclusion seems justified that the true composition of erythrosin is  $\text{C}_{20}\text{H}_6\text{O}_8\text{I}_4\text{Na}_2\cdot\text{H}_2\text{O}$  and that it is almost impossible to dehydrate it beyond this point without risk of decomposition. G. F. M.

**The Semi-pinacolinic Transformation of Alkylhydrobenzoins: Influence of the Alkyl Groups.** MARC TIFFENEAU and ALEX. OREKHOFF (*Compt. rend.*, 1922, 175, 964—967; cf. Meerwein, A., 1920, i, 2; Orekhoff and Tiffeneau, A., 1922, i, 458).—The transformation of alkylhydrobenzoins under the influence of concentrated sulphuric acid may take place in two different ways, yielding either a phenyl  $\alpha$ -alkylbenzyl ketone or a benzhydryl alkyl ketone, and the authors have investigated the influence of the nature of the alkyl group on the relative proportions of the resulting products. The conclusion is drawn that alkyl groups such as methyl, isobutyl, and phenyl, which have a strong "saturation capacity" (Meerwein, *loc. cit.*) yield the former type of product, and conversely. The groups of intermediate "saturation capacity"—ethyl, butyl, propyl, isoamyl—form hydrobenzoins which yield on dehydration mixtures of the two possible products. The results show that the influence of the alkyl group may render the secondary less stable than the tertiary hydroxyl group. This property is evident only in presence of concentrated sulphuric acid, and may result from a temporary linking of the acid with the secondary group. H. J. E.

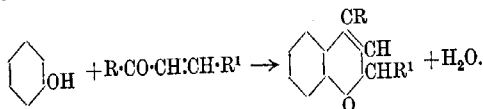
**The Action of Alcohols on Phenyl  $\alpha$ -Bromostyryl Ketone. Formation of Various Saturated and Ethylenic Compounds.**

JH. DUFRAISSE and P. GÉRALD (*Bull. Soc. chim.*, 1922, [iv], 31, 1285—1304).—Phenyl  $\alpha$ -bromostyryl ketone readily unites with alcohols in presence of small quantities of the corresponding sodium alkoxide, giving  $\alpha$ -bromo- $\beta$ -alkoxybenzylacetophenones of the general formula  $\text{COPh}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{OR}$ , which can be isolated if the reaction is conducted within suitable narrow limits of temperature, but which when warmed with the reaction mixture, lose hydrogen bromide, giving phenyl  $\beta$ -alkoxystyryl ketones,  $\text{COPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{OR}$ .

The course of the reaction and the nature of the product initially obtained by Wislicenus (A., 1900, i, 37) by the action of alcoholic potassium hydroxide on phenyl  $\beta$ -bromostyryl ketone, is thus elucidated. The phenyl  $\beta$ -alkoxystyryl ketones are obtained with even greater facility and in purer condition by the addition of alcohol to benzoylphenylacetylene in presence of sodium alkoxide. All attempts to prepare the two stereoisomerides which are theoretically possible in the case of both the saturated and unsaturated compounds, or to prepare derivatives from secondary alcohols or phenols, failed. The preparation and properties of the following compounds are described. Phenyl  $\alpha$ -bromo- $\beta$ -ethoxystyryl ketone,

m. p. 60–61°, b. p. 182–183°/3–4 mm., white crystals, readily decomposed by alkalis and hydrolysed to dibromobenzylacetophenone by hydrobromic acid. *α*-Bromo-*β*-methoxybenzylacetophenone, white crystals, m. p. 76–77°. *α*-Bromo-*β*-propoxybenzylacetophenone, m. p. 95–96°. *α*-Bromo-*β*-butoxybenzylacetophenone, m. p. 81–82°. *α*-Bromo-*β*-isobutoxybenzylacetophenone, m. p. 110–111°. *Phenyl β-ethoxystyryl ketone*, yellowish-white crystals, m. p. 77–78°, b. p. 209°/5 mm., readily hydrolysed to dibenzoylmethane by boiling with 15% alcoholic hydrogen chloride. *Phenyl β-methoxystyryl ketone*, whitish-yellow crystals, m. p. 65–66°. *Phenyl β-propoxystyryl ketone*, m. p. 59–60°. *Phenyl β-butoxystyryl ketone*, a yellow oil, b. p. 204–206°/2 mm. *Phenyl β-isobutoxystyryl ketone*, yellowish crystals, m. p. 55–56°. *Phenyl β-isopropoxystyryl ketone*, crystals, m. p. 49–50°, b. p. 180–183°/2–3 mm. G. F. M.

**Preparation of Condensation Products of  $\alpha\beta$ -Unsaturated Ketones and Phenols.** CHEMISCHE FABRIKEN VORM. WEILERTER MEER (D.R.-P. 357755; from *Chem. Zentr.*, 1922, iv, 890–891).— $\alpha\beta$ -Unsaturated ketones, in the presence of acids, or their acid additive products are condensed with phenols. The reaction in the case of the unsaturated ketones is as follows:



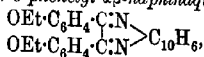
With reactive phenols such as resorcinol or *N*-substituted *m*-amino-phenols the reaction is almost quantitative. The compound from the condensation of phenol and styryl methyl ketone is a grey powder. The compound from resorcinol and styryl methyl ketone is a yellow powder. The compound from the hydrogen chloride additive product of phenyl styryl ketone (3-chloro-1-keto-1:3-diphenylpropane) and resorcinol has a red colour; it forms an acetyl derivative (annexed formula). Other condensation products are formed from phenyl *m*-hydroxystyryl ketone and pyrogallol (brown); from phenyl styryl ketone and pyrogallol (bluish-grey); from phenyl *p*-dimethylaminostyryl ketone and *m*-dimethylaminophenol (greyish-blue); from resorcinol and thiodiketobenzylidenethiazolidine (reddish-brown); from styryl methyl ketone and *p*-cresol (light brown); from *p*-acetamidophenyl *o*-chlorostyryl ketone and quinol (reddish violet). G. W. R.

**Crystallographic Study of  $\alpha\gamma$ -Diketohydrindene.** ANGELO PICCHETTO (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 143–146).— $\alpha\gamma$ -Diketohydrindene,  $d_{25}^{20}$  1.37, forms crystals belonging to the bipyramidal tetragonal class of the tetragonal system,  $a:c=1:0.9414$ . T. H. P.

***o*-Quinones and 1:2-Diketones. VI.  $\psi$ -Benzils. II. Benzils of the Peroxide Type: 2:2'-Diethoxybenzil, a Derivative of Benzil which is Colourless in Solution.** A. SCHÖNBERG and W. MALCHOW (*Ber.*, 1922, 55, [B], 3746—3752).—In a previous communication (Schönberg and Kraemer, A., 1922, i, 663), the isolation of a number of colourless solid benzils has been described which give more or less intensely coloured solutions.

The superoxide structure,  $\begin{array}{c} \text{O} \cdot \text{CR} \\ | \\ \text{O} \cdot \text{CR} \end{array}$ , has been assigned to the colour-

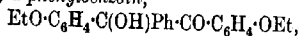
less, and the diketonic structure to the coloured benzils. This conception is strengthened by the observation that the faintly coloured solutions react less readily than those which are intensely coloured with the usual reagents for 1:2-diketones. In 2:2'-diethoxybenzil, colourless, quadratic leaflets, m. p. 157°, the authors have now found a substance which not only is colourless when solid, but also yields colourless solutions in cold alcohol, acetic acid, benzene, and light petroleum (b. p. 100—110°), which become pale yellow when heated. It melts to a dark yellow liquid which re-solidifies to colourless crystals. It is unimolecular in its colourless solutions, so that the absence of colour cannot be attributed to polymerisation. It is an unusually stable compound which is indifferent to concentrated aqueous ammonia under pressure and is not affected by hydrogen peroxide in acid or alkaline solution. It does not react with naphthylenediamine hydrochloride in boiling glacial acetic acid, but in the presence of boiling dimethylaniline it is slowly converted into 2:3-di-*o*-phenetyl- $\alpha\beta$ -naphthaquinoxaline,



colourless, pointed prisms, m. p. 180°. Similarly, 2:2'-dimethoxybenzil is transformed by *o*-phenylenediamine hydrochloride in the presence of boiling dimethylaniline into 2:3-di-*o*-anisylquinoxaline, colourless, quadratic prisms, m. p. 183°, by 3:4-diaminotoluene hydrochloride into 2:3-di-*o*-anisyl-6-methylquinoxaline, colourless prisms, m. p. 135°, and by naphthalene-1:2-diamine hydrochloride into 2:3-di-*o*-anisyl- $\alpha\beta$ -naphthaquinoxaline, colourless prisms, m. p. 180°. The method of condensation appears to be of general applicability.

2:2'-Dimethoxybenzil is reduced by amalgamated zinc and concentrated hydrochloric acid to  $\alpha\beta$ -di-*o*-anisylethane, m. p. 86° (cf. Späth, A., 1914, i, 1).

4:4'-Diethoxy- $\alpha$ -phenylbenzoin,



colourless needles, m. p. 111°, is prepared by the addition of an ethereal suspension of 4:4'-diethoxybenzoin to an ethereal solution of magnesium phenyl bromide.

3:3'-Dimethoxybenzoin, colourless prisms, m. p. 55°, obtained by the action of potassium cyanide on *m*-methoxybenzaldehyde, is oxidised by Fehling's solution in boiling aqueous alcohol to 3:3'-dimethoxybenzil, yellow prisms, m. p. 83°. The latter substance is converted by *o*-phenylenediamine hydrochloride in the

usual manner into 2:3-di-m-anisylquinoxaline, colourless leaflets, m. p. 110°. H. W.

**o-Quinones and 1:2-Diketones.** VII.  $\psi$ -Benzils. III. Separation of a 1:2-Diketone into its Coloured Crystalline Ketonic and its Colourless Crystalline Peroxide Form. A. SCHÖNBERG and W. BLEYBERG (*Ber.*, 1922, 55, [B], 3753—3758; cf. A., 1922, i, 163, and preceding abstract).—4:4'-Dibenzyl-oxybenzil has been prepared in coloured and colourless forms.

A solution of 4:4'-dihydroxybenzil in absolute alcohol is treated with the calculated quantity of potassium ethoxide and a slight excess of benzyl bromide whereby the diketonic form of 4:4'-dibenzyl-oxybenzil is obtained as dark yellow prisms, m. p. 126°. If the hot, concentrated solution of the dibenzyl ether in alcohol, glacial acetic acid, or light petroleum (b. p. 100—110°) is suddenly cooled by immersion in ice-water, the colourless peroxide variety,  $\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{Ph}$ , m. p. about 124° after becoming distinctly yellow at 121°, separates. The success of the isolation depends greatly on the rapidity with which the cooling is effected, so that it is only possible to work with small quantities at a time. A further essential condition is that the mother-liquor should be removed as rapidly as possible, since, although the colourless form is stable when dry, it rapidly passes into the yellow variety when in contact with solvents; this change occurs with such rapidity that the colourless compound appears to yield immediately coloured solutions.

4:4'-Dibenzyl-oxydibenzyl is rapidly converted by hydrogen peroxide in boiling alcoholic solution in the presence of sodium hydroxide into *p*-benzyl-oxybenzoic acid, m. p. 189° (cf. Cohen and Dudley, T., 1910, 97, 1732). It is converted by naphthalene-1:2-diamine hydrochloride in the presence of boiling dimethyl-aniline into the corresponding naphthaquinoxaline,  $\text{C}_{38}\text{H}_{28}\text{O}_2\text{N}_2$ , prisms, m. p. 156°. H. W.

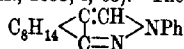
**The Acylamidoanthraquinones as Vat Dyes.** E. GRAND-MOUGIN (*Compt. rend.*, 1922, 175, 970—973).—The introduction of acyl groups into aminoanthraquinones results in the formation of a series of substances the tinctorial characters of which depend on the nature of the substituent entering the amid-group. If a hydroxyl group, which acts as an auxochrome, is present in addition, acetylation or benzylation of this group brightens the colour but usually diminishes the value of the substance as a dye. In the case of  $\alpha$ -benzamidoanthraquinone, the colour is changed from bright yellow to deep rose by the introduction of a hydroxyl group in the para position and to scarlet by a methoxyl group. Further addition of benzamido-groups results in a deepening of the colour. Isomerism influences the colour and, in addition, the tinctorial properties; the author states that no adequate explanation of these facts has yet been put forward. The following substances, all crystalline and of high m. p., were prepared; their colours and the tints they impart to vegetable fibres are noted: 4-Benzamido-

1-hydroxyanthraquinone, red, deep red. 4-Benzamido-1-acetoxyanthraquinone, yellow, rose. 4-Acetamido-1-acetoxyanthraquinone, brownish-red, light brown. 4-Benzamido-1-benzoylanthraquinone, orange-yellow, pale rose. 4-Benzamido-1-methoxyanthraquinone, orange-yellow, scarlet. 4-Acetamido-1-methoxyanthraquinone, orange-yellow, light salmon. 1:4-Diacetamidooanthraquinone, orange-yellow, light brown. 1:4-Dibenzamidooanthraquinone, reddish-yellow, reddish-yellow. 1:5-Dibenzamido-8-hydroxyanthraquinone, red, red. 1:5-Dibenzamido-4:8-dihydroxyanthraquinone, violet-blue, violet-blue. 1:5-Dianisamido-4:8-dihydroxyanthraquinone, violet-blue, violet-blue. 4:5-Dibenzamido-1:8-dihydroxyanthraquinone, violet-blue, light violet. 1:5-Diacetamido-4:8-dihydroxyanthraquinone, orange-brown. 1:5-Diacetamido-4:8-diacetoxyanthraquinone, brownish-yellow. 4:5-Diacetamido-1:8-diacetoxyanthraquinone, reddish-brown. 4:5-Dibenzamido-4:8-diacetoxyanthraquinone, yellowish-brown. The tinctorial colours of the four last-named are not stated. H. J. E.

The Investigation of *meso*-Thioanthracene Derivatives.  
I. Observations on the Production of Dithioanthraquinone, Dithiodianthrone, and Other Closely Related Derivatives.  
ISIDOR MORRIS HEILBRON and JOHN STANLEY HEATON (T., 1923, 123, 173—185).

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. IV. Methylencamphorphenylhydroxylamine. H. RUPE and W. DIEHL (*Helv. Chim. Acta*, 1922, 5, 906—922).—The reduction of methylenecamphorphenylhydroxylamine to anilinemethylene-camphor (cf. A., 1921, i, 426) can be accomplished by means of sodium hydrogen sulphite in aqueous alcoholic solution. When methylenecamphorphenylhydroxylamine is treated with thionyl chloride in ethereal solution, methylenecamphorphenylchloroamine is formed; it crystallises in short, yellowish-white prisms, m. p. 102—103°. The chlorine appears to be firmly attached to the nitrogen atom; that it has not wandered into the phenyl group was shown by condensing hydroxymethylenecamphor with *p*-chloroaniline, when *p*-chloroanilinomethylenecamphor was obtained, which crystallises in small, white prisms, m. p. 167—169°. Methylenecamphorphenylhydroxylamine combines with 1 mol. of hydrobromic acid to form a hydrobromide,  $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CH} \\ \diagdown \end{smallmatrix} \text{Br} \cdot \text{NPh} \cdot \text{OH}$ , yellow needles,

m. p. 121° (decomp.). Similarly, it readily combines with bromine in glacial acetic acid solution to form a dibromide, yellow needles, m. p. 117° (decomp.). When the hydroxylamine compound is heated with phenylhydrazine in glacial acetic acid, phenylhydroxylamine is removed and a derivative formed which was found to be identical with the phenylcamphoprazole described by Bishop, Claisen, and Sinclair (A., 1895, i, 634). The formula

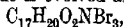


is to be preferred to that given by those authors, in which the phenyl group is attached to the 1-nitrogen atom. By the action of semicarbazide on methylenecamphorphenylhydroxylamine, the simple semicarbazone of hydroxymethylenecamphor is formed. Its m. p. is 205–206°, not 217–218° as given by Wallach (A., 1904, i, 106).

The oxidation product of methylenecamphorphenylhydroxylamine obtained by boiling it with cupric acetate (A., 1921, i, 425) can be obtained in much better yield by oxidising in cold alcohol with potassium ferricyanide. It crystallises in monoclinic needles or prisms,  $a : b : c = 0.9971 : 1 : 1.065$ ;  $\beta = 103^\circ 50'$ . Its properties

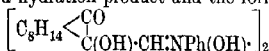
agree with the double formula,  $\left[ \text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{CH}\cdot\text{N} \begin{array}{c} \text{O} \\ \text{CO} \end{array} \\ \text{Ph} \end{array} \right]_2$ . Its form-

ation requires one atom of oxygen to two molecules of the hydroxylamine. The double molecule takes up four atoms of bromine to form a tetrabromide,  $\text{C}_{34}\text{H}_{40}\text{O}_4\text{N}_2\text{Br}_4$ , which decomposes when heated. When a solution of the tetrabromide in chloroform is warmed, hydrogen bromide is evolved and a compound,



crystallises; white, lustrous aggregates of needles, m. p. 205–208° (decomp.). From the chloroform solution of the tetrabromide a dibromide was also obtained,  $\text{C}_{34}\text{H}_{38}\text{O}_4\text{N}_2\text{Br}_2$ , m. p. 123–126° (decomp.). All these bromo-derivatives are very unstable.

When the above oxidation product of methylenecamphorphenylhydroxylamine is dissolved in 75% sulphuric acid, and then precipitated by dilution, a new compound,  $\text{C}_{34}\text{H}_{44}\text{O}_6\text{N}_2$ , is obtained. It appears to be a hydration product and the formula



is suggested for it. It has no sharp melting point, but sinters from 170°, decomposing at 190–195°. Molecular-weight determinations in different solvents gave very discordant results. It forms a methyl derivative,  $\text{C}_{33}\text{H}_{52}\text{O}_6\text{N}_2$ , m. p. 226–228°. The above formula expresses the fact that the compound is a stronger acid than the parent substance, dissolving readily in barium hydroxide solution.

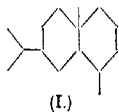
There is a possibility that in the condensation of hydroxymethylenecamphor with phenylhydroxylamine, intramolecular change occurs to give a *p*-aminophenol derivative. This has been disproved by condensing *p*-aminophenol with hydroxymethylenecamphor. The product could not be crystallised, but when methylated with methyl sulphate gave *p*-anisidinomethylenecamphor, white leaflets, m. p. 169–172°. It also gave an acetyl derivative, white leaflets, m. p. 221–223°. E. H. R.

**Action of Sulphur and certain Compounds of Sulphur on Terpenes.** P. F. BUDNIKOV and E. A. SCHILOV (*Ber.*, 1922, 55, [B], 3848–3853; cf. A., 1922, i, 944).—Pinene or mixtures of limonene and silvestrene are converted by prolonged boiling with sulphur into a viscous, reddish-brown liquid from which a homo-

geneous substance could not be isolated by fractional distillation; the percentage of sulphur in the various fractions increases with increasing boiling point. The products yield unstable precipitates when mixed with the chlorides of mercury, gold, or platinum, lead acetate or arsenic iodide in the presence of acetone or alcohol, but these are not suitable for analysis. The action of methyl iodide on the fractions gives *methyl terpenesulphinium iodide*,  $C_{10}H_{16}S,CH_3I$ , a microcrystalline precipitate, m. p. about  $121^\circ$  after previous darkening (the constant is given with reserve by reason of the lack of uniformity of the original material). The substance behaves as a typical sulphinium iodide, and is converted by moist silver oxide into the corresponding *base*. When treated with the theoretically necessary quantity of mercuric iodide in accordance with Smiles's procedure (T., 1900, 77, 163; 1907, 91, 1394), the iodide gives the compounds  $C_{10}H_{16}S,CH_3I,HgI_2$ , pale yellow, microscopic prisms, and  $C_{10}H_{16}S,CH_3I,2HgI_2$ , lemon-yellow prisms, decomp. about  $100^\circ$ . With arsenic tri-iodide, the compound  $C_{10}H_{16}S,CH_3I,AsI_3$ , dark orange-coloured crystals, is produced. The yields of the methiodide are not satisfactory, but it was not found possible to effect any improvement in the initial action by the use of aluminium chloride, mercuric chloride, or mercuric iodide as catalysts. Better results are obtained when sulphur is replaced by sulphur chloride, but the course of the change has not yet been elucidated.

The primary action of sulphur on terpenes appears to consist in the formation of a monosulphide which probably combines with a further quantity of sulphur to give polysulphides. Evidence of the formation of thio-ozonides as suggested by Erdmann has not been obtained. H. W.

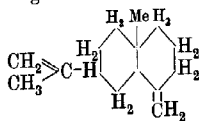
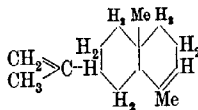
**Higher Terpene Compounds. VII. The Constitution of Eudalene, Selinene, and  $\alpha$ -Santalene. The Carbon Framework of the Sesquiterpenes.** L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1922, 5, 923-936; cf. A., 1922, i, 560).—On theoretical grounds, it seemed probable that eudalene is formed from sesqui-



terpene compounds of the type (I) by dehydrogenation and loss of a carbon atom. If this were the case, eudalene should be isomeric with the 2-methyl-8-isopropynaphthalene obtained from cadalene (A., 1922, i, 1001) and should give the same naphthalene-1:7-dicarboxylic acid as this when oxidised with dilute nitric acid. This was found to be the case. *Naphthalene-1:7-dicarboxylic acid* forms a nearly white, amorphous precipitate, sinters from  $200^\circ$ , and melts at  $265^\circ$  to a dark brown liquid. There were also obtained in small quantity a *nitro-2-methyl-8-isopropynaphthalene*, yellow needles, m. p.  $112-113^\circ$ , and a *nitronaphthoic acid*, m. p.  $225-227^\circ$ . The identity of eudalene with 1-methyl-7-isopropynaphthalene was confirmed by synthesis of the hydrocarbon as follows. Cumolol was condensed with ethyl bromoacetate by Reformatsky's method, and from the product ethyl *p*-isopropylcinnamate was obtained.

This was reduced by Bouveault's method giving *p*-isopropylphenyl-propyl alcohol,  $C_3H_7 \cdot C_6H_4 \cdot [CH_2]_2 \cdot CH_2 \cdot OH$ , b. p.  $149^\circ/12$  mm. This was converted through the bromide and cyanide into  $\gamma$ -*p*-cumyl-butyric acid,  $C_3H_7 \cdot C_6H_4 \cdot [CH_2]_3 \cdot CO_2H$ , b. p.  $186^\circ/12$  mm., crystallising in leaflets, m. p.  $31-32^\circ$ . The acid chloride is a mobile oil, b. p.  $156^\circ/12$  mm. When this chloride was treated with aluminium chloride, 8-keto-2-isopropyl-5:6:7:8-tetrahydronaphthalene was obtained, b. p.  $156^\circ/12$  mm. It forms a semicarbazone, m. p.  $195^\circ$ . This was boiled with magnesium methyl iodide, and 1-methyl-7-isopropyl-3:4-dihydronaphthalene was obtained, b. p.  $137^\circ/12$  mm. This was dehydrogenated by heating with the theoretical proportion of sulphur and gave 1-methyl-7-isopropyl naphthalene, identical with eudalene.

The constitution of eudalene having been established, it is shown that the two forms of the sesquiterpene selinene, which readily gives eudalene when treated with sulphur, probably have the following constitutions:

 $\beta$ -Selinene. $\alpha$ -Selinene.

It has now been shown that there are two types of carbon skeleton, in the sesquiterpene series, derived from three isoprene units.

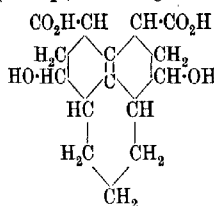
These may be called the cadinene type (II) and the eudesmol type (I). The structure of  $\alpha$ -santalene was determined by Semmler (A., 1910, i, 574), who, however, considered two formulæ possible, belonging to what he called the camphor-type and the camphene-type. It is shown that these two "types" are but different plane projections of the same three-dimensional structure. The structure is definitely related to the eudesmol type (I). It can now be concluded that all known sesquiterpenes are closely related and are derivable from a regular tri-isoprene chain of the kind present in farnesol.

E. H. R.

**The Nature of Shellac. Shellolic Acid.** C. HARRIES and W. NAGEL (*Ber.*, 1922, 55, [B], 3833-3848).—A preliminary account of partly completed work on shellac and sticklac.

The lac is freed from wax and colouring matter by successive treatment with light petroleum and water, and the residue is repeatedly agitated with ether, thereby leaving an insoluble "pure resin" which is the subject of investigation and is the vehicle of the characteristic properties of shellac. The "pure resin" is attacked by *N*-potassium hydroxide solution at the atmospheric temperature, which causes the deposition of *potassium alexisiate*, the amount being 22-24% of the resin taken. The filtrate from the salt is acidified with sulphuric acid and extracted with ether, thus yielding a mixture of shellac resin acids; these are purified

by agitating their ethereal solution with aqueous barium hydroxide and treating the latter with carbon dioxide, when the precipitated barium carbonate adsorbs a portion of the coloured resinous matter. The filtrate contains small amounts of sparingly soluble *barium aleuritate* and the freely soluble barium salts of the shellac resin acids. Attempts to isolate a homogeneous material from the latter by dialysis were not completely successful, but it is shown thereby that the salts are devoid of colour. More rapid but less complete purification can be effected through the zinc salts. The free acids do not crystallise readily. The most satisfactory results are obtained by taking advantage of the observation that the shellac resin acids, unlike other resin acids, are, at any rate in part, esterifiable by methyl-alcoholic hydrogen chloride (3%) at the atmospheric temperature, whereby *methyl shellolate*,  $C_{17}H_{24}O_6$ , long, prismatic rods, m. p.  $149^\circ$ , b. p.  $284-288^\circ/0.1$  mm. (slight decomp.),  $[\alpha]_D^{20} +32.61^\circ$  in methyl-alcoholic solution, is obtained, the amount being 8-10% of the weight of the "pure resin" taken. The ester is hydrolysed by boiling aqueous *N*-sodium hydroxide solution to *shellolic acid* (*shellenedioldicarboxylic acid*), colourless leaflets, m. p.  $199.5-201^\circ$ , decomp.  $202-203^\circ$ , which gives the Liebermann cholesterol and the Salkowski-Hesse reactions. It does not reduce Fehling's solution or decolorise a solution of bromine in chloroform; its unsaturated nature is demonstrated by its instability towards alkaline permanganate and the apparent formation of an *ozonide*. The *sodium* and *barium* salts are colourless, amorphous, and freely soluble in water; the *silver*, *copper*, and *lead* salts dissolve more sparingly. The *hydrazide*,  $C_{15}H_{24}O_4N_4$ , crystallises in well-defined prisms, m. p.  $243-244^\circ$  (decomp.); the non-crystalline *acetyl* derivative and the *diphenyldiurethane*,  $C_{21}H_{34}O_8N_2$ , m. p.  $92-94^\circ$  (decomp.) according to the rate of heating, are described. The



annexed formula for shellolic acid is suggested tentatively; the positions of the hydroxyl and carboxyl groups cannot yet be definitely assigned. The position of the double bond accounts for the inactivity of the acid towards bromine.

The non-crystalline residue of esters from which methyl shellolate has been separated (*v.s.*) has b. p.  $180-210^\circ/0.1$

mm., and appears to consist of compounds of hydroxy-acids. The latter are themselves amorphous, but give solid phenylurethanes.

The investigation has rendered it very improbable that shellac resin is the aleuritic ester of a higher alcohol, since no trace of the latter could be detected and it must be present in considerable quantity if it were an actual constituent. Since it is established that the resin does not contain a free acid, it appears probable that the shellac molecule is composed of hydroxy-acids which are united in the form of lactides. For one of the simpler components, the constitution  $\text{CO} > \text{C}_{13}\text{H}_{16}(\text{OH})\text{CO}\text{O}\text{C}_{15}\text{H}_{28}(\text{OH}) < \text{CO}$  is sug-

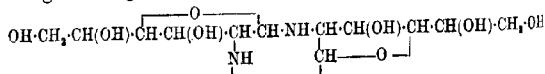
gested, the composition of which is very similar to that of the "pure resin."  
H. W.

**Centaureidin, a Decomposition Product of Centaurein, the Glucoside of Roots of *Centaurea Jacea*.** M. BRIDEL and G. CHABAUX (*Compt. rend.*, 1922, **175**, 1168—1170).—Centaureidin,  $C_{18}H_{16}O_8$  (this vol., i, 50), crystallises from 50% alcohol in microscopic, yellow needles containing water of crystallisation which is lost at 50°. The crystals melt at 197°, the anhydrous substance at 203°. It is insoluble in water, but dissolves in many organic solvents. With aqueous alkalis or sulphuric acid, it gives a golden-yellow solution. As the result of a general study of its properties, the authors suggest that it may be a flavone derivative, although the evidence on behalf of such a conclusion is mainly negative.  
H. J. E.

**Polysaccharides. XVII. Chitin.** P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1922, **5**, 832—852).—To determine how the glucosamine residues are combined in chitin, a study was made of the decomposition products obtained when chitin was distilled with zinc dust. From 300 g. of chitin from lobster shells, 37 g. of a brown oil were obtained which consisted chiefly of pyrrole compounds with a small quantity of pyridine bases, among which  $\alpha$ -picoline was identified. From the mixture of pyrrole compounds a fraction was isolated which was identified as 2-methyl-1-*n*-hexylpyrrole. This compound and 2:5-dimethyl-1-*n*-amylpyrrole were synthesised for comparison with the compound from chitin, to which the name chitopyrrole is applied.

2:5-Dimethyl-1-*n*-amylpyrrole was prepared by heating acetonol-acetone with *n*-amylamine. It is a colourless oil, b. p. 225—227°, with an orange-like odour, and gives a cherry-red, pine-shaving reaction. 2-Methyl-1-*n*-hexylpyrrole was prepared from potassium 2-methylpyrrole and *n*-hexyl iodide. It is a colourless oil, rapidly turning brown, b. p. 200—210°, smelling like old fungus, and gives an intense red, pine-shaving reaction. Chitopyrrole boils over a somewhat wider range than 2-methyl-1-*n*-hexylpyrrole, 190—220°, but essentially the two appear to be identical. Both are oxidised by chromic or nitrous acid to a substituted maleinimide, which when hydrolysed gives maleic acid and *n*-hexylamine. The last was identified by preparation of the *picrolonate*, m. p. 188—189°, which was also prepared from synthetic *n*-hexylamine.

The formation of 2-methyl-1-*n*-hexylpyrrole from chitin indicates the presence in the latter of two glucosamine residues combined through a nitrogen atom as in the following formula:



Neither the position of the acetyl groups nor the number of glucosamine residues present in the molecule can yet be stated. Chitosan, which is formed from chitin by hydrolytic removal of the acetyl groups, is converted by nitrous acid into a reducing sugar with

total loss of its nitrogen in the elementary form. This behaviour is quite in accordance with the above representation of chitin as an aldehyde-ammonia derivative.

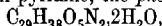
E. H. R.

**Betulin.** OTTO DISCHENDORFER (*Ber.*, 1922, 55, [B], 3692—3693).—A preliminary account of the author's observations induced by the recent publication of Schulze and Pieroh (*A.*, 1922, i, 1045).

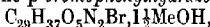
*Monobromobetulin*, m. p. 215°, and the corresponding *diacetate*, m. p. 193°, have been prepared. Analyses of the latter indicate the possibility of the formulae  $C_{30}H_{48}O_2$  or  $C_{36}H_{50}O_2$  for betulin, whereas Schulze and Pieroh (*loc. cit.*) regard  $C_{32}H_{52}O_2$  or  $C_{33}H_{54}O_2$  as probable.

H. W.

**Strophanthin. I. Strophanthidin.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1922, 54, 253—261).—When dried in a vacuum at 110° over phosphoric oxide, strophanthidin decreases in weight by an amount corresponding with the loss of  $\frac{1}{2}H_2O$ . The anhydrous substance therefore has the formula  $C_{23}H_{33}O_6$ . The loss of  $1\frac{1}{2}H_2O$  noted by Windaus and Hermanns (*A.*, 1915, i, 704, 705) was evidently due to partial decomposition. A final decision between the  $C_{23}$  formula and the  $C_{27}$  formula of Feist is rendered possible by the preparation of the *p-bromobenzoate*,  $C_{30}H_{35}O_7Br.H_2O$ . In the anhydrous condition this compound has m. p. 222—224° (decomp.),  $[\alpha]_D^{25} + 42^\circ$  in acetone. Strophanthidin (strophanthidinic acid lactone of Feist, *isomymarigenin* of Windaus and Hermanns) has the same formula as trophanthidin, crystallises with  $\frac{1}{2}H_2O$ , and forms a *benzoate*,  $C_{30}H_{35}O_7$ , rosettes of microscopic leaflets, m. p. about 270° after intering,  $[\alpha]_D^{25} + 38.0^\circ$  in chloroform. When reduced with hydrogen in the presence of colloidal palladium, strophanthidin slowly absorbs two atoms of hydrogen with the formation of *dihydrostrophanthidin*,  $C_{23}H_{34}O_6$ , which melts at 190—195° when anhydrous and crystallises with one or two molecules of water, according to the method of crystallisation. The dihydrate has  $[\alpha]_D^{25} + 34.85^\circ$  in methyl alcohol. Dihydrostrophanthidin forms a *benzoate*,  $C_{30}H_{38}O_7$ , minute, glistening prisms, m. p. 225—227° (decomp.). The presence of a carbonyl group in strophanthidin is shown by the preparation of the *oxime*,  $C_{23}H_{33}O_6N$ , glistening prisms, m. p. 270—275° (decomp.),  $[\alpha]_D^{25} + 71.3^\circ$  in pyridine, the *phenylhydrazone*,



glistening prisms, m. p. 230—232° after sintering at 175°,  $[\alpha]_D^{25} - 5.0^\circ$  in chloroform, and the *p-bromophenylhydrazone*,



pointed prisms which soften at 180—185° and become completely molten at 200°, and have  $[\alpha]_D^{25} + 105.5^\circ$  in chloroform.

E. S.

[**Catechin.**] M. NIERENSTEIN (*Ber.*, 1922, 55, [B], 3831—3833).—A reply to Freudenberg (*A.*, 1922, i, 756).

The author maintains that catechin-carboxylic acid can be prepared according to his method, and promises further details with regard to Kostanecki's catechone. With respect to the production

of optically active catechin from inactive catechin-carboxylic acid, the inactivity of the latter is maintained, but the optical activity of Gambier catechin is not considered to be established. Pure Gambier- and aca-catechins are not precipitated by solutions of gelatin. Freudenberg's observation that tetramethylcatechin cannot be demethylated by the author's method is correct so far as the derivative of Gambier catechin is concerned, but is not true for that of aca-catechin. The identity of the methylated product of the reduction of catechin with pentamethoxy- $\alpha$ -diphenylpropane is not regarded as established. The homogeneity and optical inactivity of aca-catechin, m. p. 204—205°, is maintained.

H. W.

**Tannins and Similar Compounds. XII. The Tannin of the Native [German] Oak.** KARL FREUDENBERG and ERICH VOLLBRECHT (*Annalen*, 1922, 429, 284—317).—A more expanded account of work already published (cf. A., 1922, i, 1046).

C. K. I.

**Constitution of Thiophen.** WILHELM STEINKOPF [with HALVARD AUGESTAD-JENSEN and HANS DONAT] (*Annalen*, 1922, 430, 78—112).—The lability of the hydrogen atoms in the thiophen nucleus is well illustrated by its behaviour towards cyanogen bromide, with which it reacts analogously to compounds of the type of ethyl acetoacetate and ethyl malonate, which are known to contain labile hydrogen.

Thus ethyl acetoacetate and cyanogen bromide react, giving ethyl  $\gamma$ -bromoacetoacetate. Ethyl malonate yields ethyl bromo-malonate. Acetophenone yields  $\omega$ -bromoacetophenone, and in a similar way 2-acetothienone yields  $\omega$ -bromo-2-acetothienone. Phenol and cyanogen bromide yield *p*-bromophenol, whilst indene and cyanogen bromide give 1-bromo-2-hydroxyhydrindene.

Thiophen reacts with cyanogen bromide, giving bromothiophen, b. p. 151—151.5°, and dibromothiophen, b. p. 195—206°, and with cyanogen iodide, giving 2-iodothiophen (identified as the 5-iodo-2-mercurichloride). Bromothiophen is converted by cyanogen bromide into dibromothiophen, and 2-thiotolen into bromo-thiotolen, b. p. 173—177°.

Alkylthiophens in which both  $\alpha$ -positions are substituted are also brominated by cyanogen bromide. 2:5-Dipropylthiophen yields 3-bromo-2:5-dipropylthiophen, b. p. 130—132.5°/10 mm., and 2-ethyl-5-isoamylthiophen yields 3-(or 4)-bromo-2-ethyl-5-isoamylthiophen, b. p. 122—127°/14 mm.

The above 2:5-dialkylthiophens were synthesised by way of the corresponding ketones. 5-Ethyl-2-propiothienone, b. p. 137—138°/19 mm., prepared from 2-ethylthiophen, propionyl chloride, and phosphoric oxide, gives a semicarbazone, m. p. 195—196°, and on reduction with zinc and hydrochloric acid gives 2-ethyl-5-propylthiophen, b. p. 196—197°. 5-Propyl-2-propiothienone, b. p. 137—138.5°/13 mm., prepared from 2-propylthiophen, propionyl chloride, and either phosphorus pentoxide or aluminium chloride, yields a semicarbazone, prisms, m. p. 174—175°, and on reduction

gives 2:5-dipropylthiophen, b. p. 213—214°. 5-isoAmyl-2-acetothienone, b. p. 149—151°/13 mm., prepared from 2-isoamylthiophen, acetyl chloride, and phosphorus pentoxide, gives a semicarbazone, leaflets, m. p. 212°, and on reduction yields 2-ethyl-5-isoamylthiophen, b. p. 103.5—106.5°/12 mm. None of these 2:5-dialkylthiophens gives well characterised mercury compounds on treatment with mercuric chloride. C. K. I.

**The Thiophen Series. XV. Cyclic Mercury Compounds, and Experiments on the Formation of Mixed Thiophen-Mercury Compounds.** WILHELM STEINKOPF, WILHELM BIELENBERG, and HALVARD AUGESTAD-JENSEN (*Annalen*, 1922, **430**, 40—78).—The experiments carried out with the object of preparing the mixed mercury compound,  $C_6H_5S\cdot HgPh$ , were based on the reaction between magnesium phenyl bromide and phenyl mercurichloride, the products of which are mercury diphenyl and magnesium chloride and bromide. Pure mercury phenyl thienyl could not be isolated from the product of the action of magnesium phenyl bromide in 2-thienylmercurichloride, although evidence of its formation was obtained. Mercury diphenyl is also formed by the action of mercurous chloride on magnesium phenyl bromide, and by the action of stannous chloride on magnesium phenyl chloride. Similarly, mercury 2:2'-dithienyl is the product of the reduction of thienyl-2-mercurichloride by stannous chloride.

A series of cyclic mercury-thiophen compounds is described of which dimercury 2:2':5:5'-dithienylene,  $\begin{array}{c} CH_3C-Hg-C_6H_5 \\ | > S S < | \\ CH_3C-Hg-C_6H_5 \end{array}$ , is

typical. This substance is obtained from 2:5-thienylenedimercurichloride and either sodium iodide or sodium thiocyanate in the presence of pyridine. Pyridine and mercuric chloride convert it into mercury 5:5'-dithienylene-2:2'-dimercurichloride, which may also be obtained by the action of pyridine on thienylene-2:5-dimercurichloride. Dimercury 3:3'-(or 4:4')diethyl-2:2':5:5'-dithienylene, mercury diethyl-5:5'-dithienylene-2:2'-dimercurichloride, and dimercury 3:4:3':4'-tetramethyl-2:2':5:5'-dithienylene are also described; like the unalkylated parent substances, they are all exceedingly insoluble compounds which do not melt at 320°. Dimercury diethyldithienylene, on treatment with mercuric chloride under regulated conditions, yields mercury diethyldithienylene-dimercurichloride, but excess of the reagent effects complete disruption of the molecule, the product being 3-ethylthienylene-2:5-dimercurichloride.

A colorimetric method of estimating the rate of separation of mercuric sulphide when an organic mercury compound is treated with sodium sulphide is described in the original. C. K. I.

**Synthesis of Substituted Thianthrens. I. Thianthren and Nitrothianthren.** SRI KRISHNA (T., 1923, **123**, 156—160).

**Production and Reactions of 2-Dithiobenzoyl.** MARY McKIBBEN and ERNEST WILSON McCLELLAND (T., 1923, **123**, 170—173).

**The Alkaloids of the Northern Aconite (*Aconitum septentrionale*, Koelle).** GUNNAR WEIDEMANN (*Arch. exp. Path. Pharm.*, 1922, 95, 166—180).—Two alkaloids, isolated from the northern aconite, have been investigated. Lappaconitine,

$C_{32}H_{42}O_9N_2$ , forms hard, glass clear, six-sided prisms, m. p.  $223^\circ$ ,  $[\alpha]_D^{25} + 27.4^\circ$  in chloroform. It is a monoacid base, and contains three methoxyl groups. It forms a *chloroplatinate*,  $C_{32}H_{42}O_9N_2 \cdot HPtCl_5$ , and a *chloraurate*,  $C_{32}H_{42}O_9N_2 \cdot HAuCl_4$ . On hydrolysis with alcoholic potash, it yields lappaconitic acid,  $C_8H_9O_3N$ , shown to be acetyl anthranilic acid, and a base lappaconine,  $C_{23}H_{35}O_7N \cdot 2H_2O$ , m. p.  $93^\circ$ ,  $[\alpha]_D^{25} + 22.41^\circ$ . It forms a *hydrochloride*,  $C_{23}H_{35}O_7N \cdot HCl$ , large, colourless crystals. Septentrionaline,  $C_{29}H_{34}O_6N_2(OMe)_4$ , the other alkaloid investigated, is an amorphous, white powder, m. p.  $131^\circ$ ,  $[\alpha]_D^{25} + 32.71^\circ$ , forming a *chloroplatinate*,  $C_{29}H_{34}O_6N_2 \cdot HPtCl_5$ . On hydrolysis with alcoholic potash, there is obtained (1) an acid,  $C_8H_9O_3N$ , m. p.  $125$ — $126^\circ$ , which when boiled with sodium hydroxide solution yields anthranilic acid, losing  $CH_2O$ , and (2) a base,  $C_{25}H_{33}O_7N$ , m. p.  $89^\circ$ ,  $[\alpha]_D^{25} + 29.55^\circ$ , forming a *hydrochloride*,  $C_{25}H_{33}O_7N \cdot HCl$ .  
W. O. K.

**Paniculatine, the Alkaloid from *Aconitum paniculatum*, Lam.** G. E. BRUNNER (*Schweiz. Apoth. Zig.*, 1922, 60, 357—358; from *Chem. Zentr.*, 1922, iii, 1007).—Paniculatine,  $C_{29}H_{35}O_7N$ , the alkaloid from *Aconitum paniculatum*, Lam., is not identical with aconitine. It forms small, rhombic prisms with m. p.  $263^\circ$ .  
G. W. R.

**Melanins, Arising from Adrenaline.** PIETRO SACCARINI (*Biochem. Z.*, 1922, 132, 439—442).—Melanin-like pigments, obtained by the oxidation of adrenaline with chlorine water, are described.  
W. O. K.

**Preparation of a Quinine Derivative.** AKTIEN-GESellschaft FÜR ANILIN-FABRIKATION, JULIUS ALTSCHUL, and MARCELL BACHSTEZ (D.R.-P. 357753; from *Chem. Zentr.*, 1922, iv, 951).—Equimolecular amounts of quinine and 4-ethoxyphenylmalonamic acid are fused together and crystallised from hydrolysing solvents or allowed to react as such or in form of their salts in the presence of hydrolysing solvents. *Quinine 4-ethoxyphenylmalonamate* forms long, colourless needles, m. p.  $72$ — $73^\circ$ .  
G. W. R.

**Quiteninone.** SIGMUND FRÄNKEL, CHARLOTTE TRITT-ZIEMING and LILY GOTTESMANN-GRAUER (*Ber.*, 1922, 55, [B], 3931—3935).—The action of hydrogen peroxide (30%) on a solution of quinine sulphate in dilute sulphuric acid in the presence of copper or ferric sulphate as catalyst and at the atmospheric temperature leads to the production of *quiteninone*,  $C_{19}H_{20}O_4N_2$ , needles, m. p.  $156^\circ$ . The reaction appears to be considerably influenced by external factors and to take place through a number of intermediate products of which quinine oxide (cf. Speyer and Becker, A., 1922,

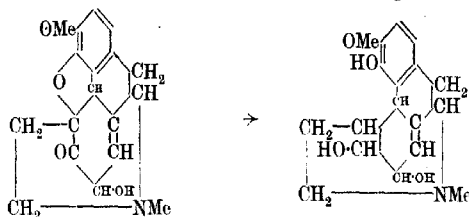
i, 674) is one. Quiteninone is also produced by the oxidation of quitenine (cf. Nierenstein, A., 1920, i, 875). It gives a *picrate*, m. p. 140°. The constitution of quiteninone is partly elucidated by the preparation of the *methyl ester picrate*,  $C_{20}H_{22}O_4N_3 \cdot 2C_6H_3O_7N_3$ , decomp. 270°, and the *methyl ester dihydrochloride*, m. p. 181°. Quiteninone could not be caused to react with phenylhydrazine, *p*-nitrophenylhydrazine, or semicarbazide hydrochloride; with hydroxylamine in alkaline solution, it gives an oxime which is identified as the corresponding *picrate*,  $C_{19}H_{21}O_4N_3 \cdot C_3H_3O_7N_3$ , m. p. 126°. H. W.

**Esterification of Creatine.** ARTHUR W. DOX and LESTER YODER (*J. Biol. Chem.*, 1922, 54, 671—673).—Saturation of a suspension of creatine in an alcohol with hydrogen chloride results in the formation, not of creatinine, but of an ester of creatine the hydrochloride of which separates on the addition of ether. By this means the author has prepared: *creatine methyl ester hydrochloride*, slender needles, m. p. 139—140°; *creatine ethyl ester hydrochloride*, needles, m. p. 163°; *creatine n-butyl ester hydrochloride*, flat needles, n. p. 138°. Each salt melts with the evolution of gas and leaves a solid residue of creatinine hydrochloride. E. S.

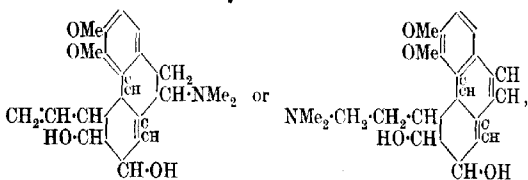
**Ergot.** A. STOLL (*Schweiz. Apoth. Ztg.*, 1922, 60, 341—346; *from Chem. Zentr.*, 1922, iii, 1007; cf. Spiro and Stoll, A., 1922, 47).—The specific effect of ergot is not considered to be due to the presence of simple amines such as tyramine. After addition of acid reagents such as aluminium sulphate to ergot, extraction of one kg. of the material with ether and benzene removes 350—400 g. of alkaloid-free ergot oil together with soluble acid and neutral substances such as organic acids, phytosterol, and colouring matters. From the acidified cell material a crystalline alkaloid was separated. *Ergotamine*,  $C_{33}H_{35}O_5N_5 \cdot 2COMe \cdot 2H_2O$  (from acetone) forms highly refractive rhombic prisms; it has  $[\alpha]_D^{25} -155^\circ$  in 0.6% chloroform solution; the monoacid base and its compounds decompose on heating at 140°; at 180° a brown mass is formed with evolution of gas. On keeping an ethyl-alcoholic solution or warming a methyl-alcoholic solution of ergotamine, an isomeride, *ergotaminine*, of weaker basic character, is formed. It crystallises in triangular leaflets and has  $[\alpha]_D^{25} +381^\circ$  in 0.6% chloroform solution. Ergotaminine may be reconverted into ergotamine. Both isomerides give a blue coloration with strong sulphuric acid. Ergotamine is unstable in air. G. W. R.

**The Hydroxycodeinone Series.** EDMUND SPEYER [with S. SELIG and MARTIN HEIL] (*Annalen*, 1922, 430, 1—40).—A further account (see A., 1915, i, 580; 1916, i, 157, 758; 1921, i, 685) of derivatives of codeine and thebaine including the reduction of hydroxycodeinone to hydroxythebainol and the conversion of the latter into a nitrogen-free substance by exhaustive methylation. All results are interpreted on the basis of Knorr's formula for morphine.

Hydroxycodeinone is converted either by electrolytic reduction or by zinc and formic acid into *hydroxythebainol*, m. p. 234° :



the *formate* of hydroxythebainol, m. p. 227°, and 7-hydroxycodeine being obtained as by-products in the latter case. Hydroxythebainol yields a crystalline *hydrochloride*, *hydrobromide*, m. p. 252—253°,  $[\alpha]_D^{20} -157.7^\circ$ , *hydriodide*, m. p. 247°, and *picrate*, m. p. 204—206°. On treatment with benzoyl chloride, it gives a *benzoyl* derivative, needles, m. p. 257°; with bromine and acetic acid, a *perbromide*, which on reduction by sulphur dioxide gives a *mono-bromo-derivative*, m. p. 230—231°, reducible to hydroxythebainol, and with hydrogen peroxide an *N-oxide*, which crystallises in prisms, m. p. 237°. On methylation with methyl sulphate and alkali, hydroxythebainol yields the *methyl ether methiodide*, rhombs, decomp. 233°, which with hot alkali hydroxide gives des-N-methylhydroxythebainol methyl ether,



small needles, m. p. 195—197°. The *hydriodide* forms needles, m. p. 255°, and the *methiodide*, obtained with the aid of methyl iodide, microscopic prisms, decomp. 239—240°. On treating this substance successively with silver oxide and concentrated alkalis, trimethylamine is eliminated and the nitrogen-free substance, 2 : 3-dihydroxy-5 : 6-dimethoxy-4-vinyl-2 : 3 : 4 : 4a-tetrahydrophenanthrene, is obtained. This forms stout prisms, m. p. 188—189°, and is insoluble in alkali, which shows that the two hydroxyl groups are in the aliphatic part of the molecule.

An improved method of preparation of hydroxythebainone is described. Its *dibromide*, obtained by the use of bromine and chloroform, decomposes at 258°, and on reduction by hydrogen and palladium black gives hydroxydihydrothebainone, which may be obtained directly from hydroxythebainone by means of the same reducing agent. The *methiodide* of hydroxythebainone forms prisms, m. p. 245°, the *acetyl* derivative, needles, m. p. 197°, and

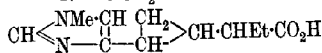
he *oxime* of the acetyl derivative, prisms, m. p. 216–218°. The *nethiodide* of the acetyl derivative decomposes at 212–213°, and gives a non-crystalline *deoxy-base* on decomposition by alkalis. The *nethiodide* of the acetyl derivative of 7-hydroxycodeine sinters at 230° and decomposes at 256°.

Reduction of hydroxycodeinone oxime by hydrogen and palladium under various conditions yielded hydroxydihydrocodeinone, and it was not found possible to prevent the elimination of the oximino-group. Parallel experiments with styrylmethylketoxime and distyrylketoxime yielded analogous results, the products being benzylacetone and dibenzylacetone, respectively. C. K. I.

**The Pilocarpine Series. II. Pilocarpic Esters and their Derivatives.** MAX POLONOVSKI AND MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], 31, 1185–1201; cf. this vol., i, 52).—Although it is generally accepted that a  $\gamma$ -lactone group is present in pilocarpine and its isomeride, few of the properties of a  $\gamma$ -lactone have been actually shown to be characteristic of these substances. The authors find that the esterification of pilocarpine by means of methyl or ethyl alcohol and hydrogen chloride does not yield the ethyl ester of pilocarpic acid but the ethyl  $\gamma$ -chloro-ester, thus confirming the  $\gamma$ -lactone grouping by the characteristic reaction of simultaneous esterification of acidic and alcoholic groups by alcohol and halogen, respectively. *Methyl  $\gamma$ -chloropilocarpate* forms small, transparent prisms, m. p. 42–44°,  $[\alpha]_D + 32.6^\circ$ , and is a strong base; the *nitrate* forms lustrous plates, m. p. 157°,  $[\alpha]_D + 20^\circ$ . *Ethyl  $\gamma$ -chloropilocarpate* was obtained as an oil,  $[\alpha]_D + 29.2^\circ$ ; the *nitrate* forms lustrous plates, m. p. 136°,  $[\alpha]_D + 23.4^\circ$ . On treatment of the nitrate with concentrated sulphuric acid, it is converted into ethyl  $\gamma$ -chloronitropilocarpate. The  $\gamma$ -chloro-esters of pilocarpine are readily relactonised with loss of the halogen atom and the alkyl group; this is accompanied by the transformation of a portion of the alkaloid into its isomeride. *isopilocarpine* behaves in a similar manner to pilocarpine on esterification. *Methyl  $\gamma$ -chloroisopilocarpate* is an oil of very alkaline reaction,  $[\alpha]_D - 7.5^\circ$ , *nitrate*, hygroscopic crystals, m. p. about 100°,  $[\alpha]_D - 5.6^\circ$ ; the *ethyl* ester is also an oil,  $\alpha_D - 5^\circ$  (*nitrate*, crystalline, m. p. 95°,  $[\alpha]_D 0$ ). All these chloro-esters are unstable, even in the solid state at the ordinary temperature, a portion of the substance being transformed into the hydrochloride of a quaternary base. The chloro-esters react readily with sodium ethoxide or methoxide, yielding an oily mixture of the ethyl esters of  $\alpha$ - and  $\beta$ -anhydropilocarpic acids, separable by the difference in solubility of their nitrates in water.  *$\alpha$ -Anhydropilocarpic acid*,  $C_{11}H_{16}O_2N_2$ , forms lustrous plates, m. p. 243°,  $[\alpha]_D - 19^\circ$ ; the *hydrochloride* has m. p. 187°; the *ethyl ester* is an oil and yields a *nitrate*, colourless needles, m. p. 165°,  $[\alpha]_D - 19^\circ$  in alcohol and  $+3.4^\circ$  in water.  *$\beta$ -Anhydropilocarpic acid* forms prismatic crystals, m. p. 186°,  $[\alpha]_D + 42^\circ$ ; the *hydrochloride* has m. p. 142°; the *ethyl ester* forms large, transparent tablets, m. p. 48°, and gives a *nitrate*, m. p. 95°,  $[\alpha]_D - 28^\circ$  in water.

On bromination, ethyl  $\alpha$ -anhydropilocarpate gives a *bromo-derivative*,  $C_{13}H_{19}O_2N_2Br$ , from which on hydrolysis the *bromo-acid*, m. p.  $139^{\circ}$ — $139^{\circ}$ , is obtained.

The formulæ  $CH \begin{smallmatrix} \diagup NMe \cdot CH \\ \diagdown N - C \cdot CH_2 \cdot CH \end{smallmatrix} \begin{smallmatrix} CH_2 \\ CH \end{smallmatrix} > CEt \cdot CO_2H$  and

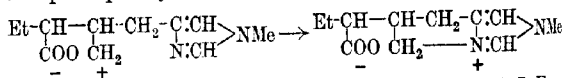


are suggested as possible for the isomeric acids.

H. J. E.

**The Pilocarpine Series. III. *iso*Pilocarpinanil or Phenyl-isopilopyrrolidone.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1201—1204; cf. preceding abstract).—Pilocarpine combines with aromatic amines yielding very stable pyrrolidone compounds. This reaction points to the existence of a lactone group in pilocarpine (cf. Emmert and Meyer, A., 1921, i, 268). The same substances may be obtained from the  $\gamma$ -halogen acids derived from the alkaloid. Prolonged heating being necessary, the products are derivatives of *isopilocarpine*. *isoPilocarpinanil* is a hard substance, slightly alkaline in reaction, which gives with mineral acids crystalline salts of acid reaction. The *nitrate*, colourless plates, m. p.  $162^{\circ}$ ,  $[\alpha]_D + 21.2^{\circ}$ , and the *hydrochloride*, white, hygroscopic prisms, m. p.  $135^{\circ}$ , were prepared. The base yields on nitration a substance containing a nitro-group in the benzene ring, which was not further investigated. H. J. E.

**The Pilocarpine Series. IV. Metapilocarpine.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1204—1208; cf. preceding abstracts).—As substances obtained by the authors from the decomposition of  $\gamma$ -chloro-esters of pilocarpine seemed to be identical with the metapilocarpine described by Pinner (A., 1905, i, 658), it appeared that the latter could not be a simple stereoisomeride. An examination of its properties resulted in confirmation of Pinner's observations. The substance is inactive towards polarised light, and, although neutral to litmus and giving with acids salts of acid reaction, does not combine with alkalis. Its reactions lead to the conclusion that in metapilocarpine the lactone grouping is absent and the acid group which replaces it is neutralised either by the basic glyoxaline ring or by a betaine linking,  $CO-O-N$ . The authors prefer the second explanation, and therefore represent the transformation of pilocarpine into metapilocarpine by



H. J. E.

**The Pilocarpine Series. V. Isomerism of Pilocarpine and *iso*Pilocarpine.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1314—1330).—The authors discuss the evidence for and against the various hypotheses advanced

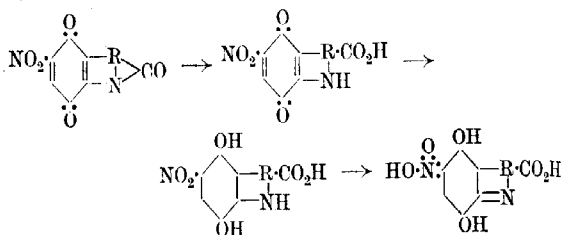
to account for the isomerism of pilocarpine and *isopilocarpine*, and reject as untenable theories based on position isomerism in favour of stereoisomerism arising in or near the lactonic group. Their conclusions are largely based on the isomerisation of pilocarpine and its derivatives to *isopilocarpine* and its corresponding derivatives by action of small quantities of sodium ethoxide on alcoholic solutions of the alkaloid in the cold. It was found that pilocarpine and nitropilocarpine were completely isomerised under these conditions by traces of sodium ethoxide, that molecular quantities of sodium ethoxide gave an isomerised and delactonised product, the de-lactonisation proceeding much more slowly than the isomerisation and requiring twenty-four to forty-eight hours for completion, and that sodium pilocarpate, sodium nitropilocarpate, and ethyl chloropilocarpate were not isomerised to the *iso*-derivatives; in other words, esterification or salt formation causes a stabilisation of the pilocarpine molecule, whence it is concluded that for isomerisation by sodium ethoxide the presence of the unchanged lactone grouping is essential, and this group is probably the seat of the isomerism. Whilst the nature of the stereoisomerism must for the present be left an open question, the authors incline to the view that it may be a case of partial racemisation of one of the two asymmetric C atoms of the lactonic group in view of the similarity between the isomerism of pilocarpine and that of hyoscyamine.

G. F. M.

**Strychnos Alkaloids. XXXV. Ethers of Hydroxydihydrobrucinolone and the Violet Colour Reaction of the Nitroquinones obtained therefrom.** HERMANN LEUCHS, JOHANNES GRÜSS, and HARRY HEERING (*Ber.*, 1922, 54, [B], 3729—3738; cf. A., 1921, i, 883).—The action of boiling methyl-alcoholic potassium hydroxide solution on brucinolone or its acetyl derivative leads to the formation of small amounts of *methoxydihydrobrucinolone*,  $C_{22}H_{26}O_6N_2 \cdot 3H_2O$ , coarse prisms or plates, m. p.  $82^\circ$ ,  $[\alpha]_D^{25} -50.3^\circ$  in glacial acetic acid solution, and (mainly) a product, m. p.  $200-202^\circ$  after softening at  $190^\circ$ , which is converted by acetic anhydride into acetylmethoxydihydrobrucinolone,  $C_{24}H_{28}O_7N_2$ , m. p.  $258-270^\circ$ ,  $[\alpha]_D^{25} -92.5^\circ$ , in glacial acetic acid solution, and acetylcryptobrucinolone. Attempts to separate the mixture, m. p.  $200-202^\circ$ , into its components by methyl-alcoholic ammonia at  $100^\circ$  were unsuccessful. Under these conditions, cryptobrucinolone is converted into a base,  $C_{21}H_{25}O_5N_3$  (isolated as the hydrochloride), identical with that isolated previously, but in much poorer yield, from crude acetylbrucinolone and ammonia (Leuchs, A., 1914, i, 317); its formation in the latter instance appears to depend on the presence of cryptobrucinolone or its ester in the acetylbrucinolone. It unites with phenylcarbimide to give the compound  $C_{28}H_{30}O_6N_4$ , small prisms, m. p.  $200^\circ$ .

Ethoxydihydrobrucinolone is converted by 5*N*-nitric acid at  $0^\circ$  into the corresponding *quinone*, a yellowish-red resin which yields a *semicarbazone*, slender, orange-coloured needles, m. p.  $240^\circ$  after change at  $211^\circ$ . The free quinone is reduced by sulphur dioxide

to a colourless, amorphous product; the corresponding acetate could not be caused to crystallise. The action of 5*N*-nitric acid on ethoxydihydrobrucinolone at 50–60° leads to the formation of the *nitroquinone hydrate*,  $C_{21}H_{25}O_9N_3$ , golden-yellow leaflets, which is further transformed into the *semicarbazone*,  $C_{22}H_{26}O_9N_6$ , slender, pale yellow needles, and the crude *monoethyl ester*. The nitroquinone hydrate is reduced by sulphurous acid to the *nitroquinol hydrate*,  $C_{21}H_{25}O_9N_3$ , an amorphous, dark violet powder, m. p. (variable) about 185° (decomp.). The latter is converted by hydrogen chloride in methyl and ethyl alcohols into the *methyl* and *ethyl* esters, amorphous, violet substances. The *triacetyl* derivative of the nitroquinol has m. p. 175–180° (decomp.). The relationships of the quinone and quinol compounds are illustrated by the scheme :



H. W.

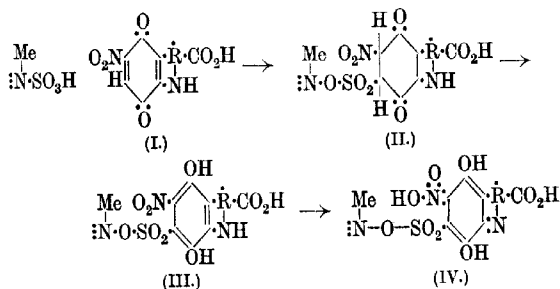
**Strychnos Alkaloids. XXXVI. The Preparation of Methoxy- and Ethoxy-dihydrostrychninolones and of Strychninolone-c; Oxidation of the Latter.** HERMANN LEUCHS and RUDOLF NITSCHKE (*Ber.*, 1922, 55, [B], 3738–3745; cf. A., 1921, i, 883; Leuchs, Grüss, and Heering, preceding abstract).—Strychninolone-*a* is converted by methyl-alcoholic potassium hydroxide solution initially into the *b*-form, and finally into an inseparable mixture of *methoxydihydrostrychninolone* and *strychninolone-c*. The former has been isolated only as a resin which is converted by sodium acetate and acetic anhydride into a crystalline *acetate*,  $C_{22}H_{24}O_9N_2$ , colourless, quadratic crystals, m. p. 237–239° after softening at 230°,  $[\alpha]_D^{20}$  –109° when dissolved in glacial acetic acid. The course of the change is followed more readily when the methyl- is replaced by ethyl-alcoholic potassium hydroxide solution, since in this instance *ethoxydihydrostrychninolone*, needles, m. p. about 100°,  $[\alpha]_D^{20}$  –51.9° in glacial acetic acid solution, m. p. (+MeOH), 65–70°, can be isolated directly.

Strychninolone-*c* is transformed by acetic anhydride and sodium acetate into *acetylstrychninolone-c*,  $C_{21}H_{20}O_4N_2$ , domatic prisms, m. p. 256–257°,  $[\alpha]_D^{20}$  –229.6° in glacial acetic acid solution. The latter substance is oxidised in acetone solution by powdered potassium permanganate to an *acid*,  $C_{21}H_{20}O_6N_2 \cdot H_2O$ , colourless prisms, m. p. 280–282° (decomp.) after softening at 260°, in which, however, the water of crystallisation appears to be retained with

unusual tenacity. The acid is converted by hydrochloric acid into acetic and oxalic acids and a non-crystalline, unstable hydrochloride. The behaviour of acetylstrychninone-*c* is closely analogous to that of cryptobrucinolone; each probably contains the oxidisable group,  $\text{CH} \begin{smallmatrix} \text{R}=\text{N} \\ \text{CH}\cdot\text{CO} \end{smallmatrix}$ , which is transformed by oxygen into  $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{N}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ .

H. W.

**Strychnos Alkaloids. XXXVII. The Degradation of Methylcacotheline and its Violet Colour-reaction with Sodium Sulphite.** HERMANN LEUCHS, BERNHARD WINKLER, and W. ROBERT LEUCHS (*Ber.*, 1922, 55, [B], 3936—3950).—Among the violet products which are formed from cacotheline and analogous substances of the brucine series, methylcacotheline methosulphite (A., 1919, i, 35) occupies a peculiar position, since it becomes isomerised when heated, with the production of a violet isomeride which is therefore not formed in the usual manner by the addition of two atoms of hydrogen. The isomerism cannot be regarded as definitely proved by analytical methods, since the presence of two additional atoms of hydrogen in the molecule does not greatly affect the composition, but it is now placed beyond doubt by the observations that the substance is produced in 50% yield by the action of one molecular proportion of sodium sulphite on two molecular proportions of methylcacotheline, that sulphuric acid is not produced thereby, and that the remainder of the methylcacotheline passes into the yellow methylbetaine (cf. A., 1920, i, 179), which is convertible by further treatment with sodium hydrogen sulphite into the violet methosulphite. The reactions which take place in the production of the violet methosulphite are indicated by the scheme:

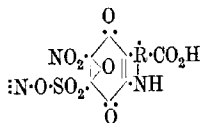


The ammonium sulphite becomes added to the quinone nucleus with the formation of a phenylsulphite ester group or a sulphonic acid, whereupon the quinone becomes isomerised to quinol without addition of extraneous hydrogen; the nitro-group subsequently passes into the *isonitro*-form with production of a new quinonoid arrangement and development of the dark colour.

The so-called violet "methosulphite" (formula IV) is converted

by drastic treatment with hydrogen chloride and ethyl alcohol into a *monoethyl ester*,  $C_{22}H_{29}O_{10}N_3S$ , dark violet prisms, and by acetic anhydride and anhydrous sodium acetate at  $100^\circ$  into an *anhydride*,  $C_{22}H_{23}O_9N_3S$  (the *ammonium salt*, orange-coloured needles, and the *diacetyl derivative*,  $C_{28}H_{47}O_{11}N_3S$ , pale yellow leaflets, are described). The sulphite,  $C_{22}H_{25}O_{10}N_3S$ , is transformed by methyl sulphate and alkali hydroxide into a *monomethyl derivative*,  $C_{23}H_{27}O_{10}N_3S$ , a blackish-violet, crystalline powder. Reduction of the violet sulphite or of the corresponding quinone with tin and hydrochloric acid has been shown previously (A., 1919, i, 36) to yield a colourless compound,  $C_{22}H_{25}O_7N_3S$ , the formation of which is now interpreted as due to the reaction of the  $:NH$  and  $\cdot CO_2H$  groups to form  $\cdot N\cdot CO\cdot$ . The main product formed by the action of sodium sulphite and sulphurous acid on the quinol from methylcatheline (A., 1920, i, 178) is the compound  $C_{22}H_{27}O_{11}N_3S_2$ , almost colourless, four-sided plates or prisms, in which the  $\cdot N\cdot CO\cdot$  group of the substance described above has become transformed into  $\cdot NH\cdot CO_2H$ , and the  $NH_2$  group into  $\cdot NH\cdot SO_3H$ . A second product,  $C_{22}H_{24}O_8N_3S$ , needles, appears to be derived from  $C_{22}H_{25}O_7N_3S$  by the conversion of the amino- into the hydroxy-group.

The violet methosulphite is converted by passing oxygen through its ammoniacal solution into a substance (cf. A., 1919, i, 35) to which the composition  $C_{22}H_{29}O_{11}N_3S$  (instead of  $C_{21}H_{23}O_{11}N_3S$ ) is now assigned, and for which the annexed structure is suggested. The substance is re-transformed into the violet methosulphite by drastic reduction with sulphurous acid, whereas, when treated with tin and hydrochloric acid, it gives the amine hydrochloride,  $C_{22}H_{25}O_7N_3S\cdot HCl\cdot 4H_2O$  (the



corresponding *sulphate*, *nitrate*, and *hydrobromide* are described), and small quantities of a compound,  $C_{22}H_{29}O_9N_3S\cdot HCl\cdot 2H_2O$ , thin prisms. Esterification of the compound  $C_{22}H_{29}O_{11}N_3S$  by methyl or ethyl alcohol in the presence of hydrogen chloride yields products which contain halogen, whereas when sulphuric acid is used the corresponding *dimethyl* compound,  $C_{24}H_{29}O_{12}N_3S$ , pale green prisms, and *diethyl derivative*,  $C_{26}H_{33}O_{12}N_3S$ , rectangular prisms, which is hydrolysed by potassium carbonate solution to the *monoethyl* compound,  $C_{24}H_{29}O_{12}N_3S$ , almost colourless, short prisms, are obtained. The dialkyl derivatives are produced by the esterification of the carboxy-group and the addition of alcohol consequent on the rupture of the ethylene oxide bridge with production of the group  $\cdot C(OH)\cdot C(OAlk)\cdot$ .

The oxidation of the violet nitroquinol by air does not therefore lead to any considerable degradation of the molecule. A more drastic change is effected when the original material, methylcatheline, is treated with a solution of bromine in hydrobromic acid. Two products are thereby obtained, the first of which, produced in 30% yield, has the formula  $C_{20}H_{25}O_6N_2Br$ , and crystallises in colourless, rectangular prisms or leaflets,  $[\alpha]_D^{25} - 6.75^\circ$  in

aqueous solution (corresponding *nitrate*, colourless needles or prisms,  $[\alpha]_D^{20} -7.4^\circ$  when dissolved in water); it appears to be analogous to the salt,  $C_{19}H_{23}O_6N_2 \cdot HBr$ , prepared by Hanssen (A., 1887, 505; cf. Leuchs, Millbrand, and Leuchs, A., 1922, i, 1052) by the action of bromine water on cacotheline. The second compound is obtained initially in unstable union with sulphurous acid, after the removal of which it has the composition  $C_{18}H_{23}O_6N_2Br_2$ ,  $[\alpha]_D^{20} -4.3^\circ$  in aqueous solution; it appears to be a *N*-methyl derivative of a dibrominated bromide.

The methyl ester of the oxime of cacotheline methochloride is converted by methyl alcoholic ammonia at  $100^\circ$  into the *methyl* ester of the *nitrosophenolmethylbetaine*,  $C_{22}H_{26}O_7N_4$ , apple-green prisms. H. W.

**Nitropyrroles.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1922, [v], 34, ii, 3—5).—Fischer and Zerweck (A., 1922, i, 758) state inaccurately that the nitration of alkylpyrroles may be effected smoothly by means of nitric acid (cf. Angeli, A., 1911, i, 397). The compounds investigated by these authors are not alkylpyrroles, but esters of carboxylic acids derived from keto-, formyl-, etc., derivatives of pyrrole, and the action on them of nitric acid consists, not in true nitration, but in replacement of acetyl, aldehyde-, methyl, etc., groups by nitro-groups. T. H. P.

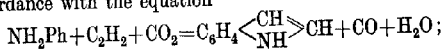
**Melanins from Pyrrole Derivatives.** PIETRO SACCARDI (*Biochem. Z.*, 1922, 132, 443—456).—A general review of the relations of melanin pigment to the pyrrole group. W. O. K.

**The Tetrachlorodipyridinoiridates.** MARCEL DELÉPINE (*Compt. rend.*, 1922, 175, 1075—1077; cf. A., 1922, i, 859).—Details of the preparation of the red and orange isomerides of potassium tetrachlorodipyridinoiridate by the action of pyridine on potassium iridichloride or potassium aquapentachloroiridate are given, together with an account of certain of their properties. The introduction of pyridine into the complex diminishes the number of acid functions and at the same time renders the substance more stable. H. J. E.

**The Reaction between Acetylene and Aniline at High Temperatures.** RIKO MAJIMA, TADASHI UNNO, and KASHICHI IINO (*Ber.*, 1922, 55, [B], 3854—3859).—The production of small quantities of indole by subjecting a mixture of acetylene and aniline to a red heat has been observed previously in the presence of aluminium oxide as catalyst. Experiments in which the latter was replaced by the oxides of silicon, iron, chromium, thorium, nickel, cobalt, manganese, molybdenum, tungsten, vanadium, or titanium, or by metallic nickel, iron, cobalt, platinum, palladium, samium, or copper, did not lead to satisfactory results; nickel was the most powerful catalyst, but speedily loses its activity. Better results are obtained by leading a mixture of aniline vapour, acetylene, and carbon dioxide through a tube heated at  $600-700^\circ$ , thereby, under the most favourable conditions, the yield of indole

amounts to 34% of the changed aniline. Benzene, carbazole, and  $\beta$ -naphthylamine are produced in considerably smaller quantity, and still smaller amounts of pyrrole, naphthalene, and quinoline are formed. Glass and porcelain tubes are unsatisfactory on account of frequent breakage, but excellent service is rendered by wide iron tubes which have been subjected to previous protracted heating at 600–650° in a current of acetylene, whereby the inner surface becomes coated with a thin, black, compact layer possibly composed of carbon.

The formation of indole and  $\beta$ -naphthylamine is probably due to the intermediate production of vinylaniline, thus:  $\text{NH}_2\text{Ph} + \text{CH}:\text{CH} \rightarrow \text{NHPh}\cdot\text{CH}:\text{CH}_2 \xrightarrow{-\text{H}_2} \text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix}\rangle\text{CH}$  and  $\text{NHPh}\cdot\text{CH}:\text{CH}_2 \rightarrow \text{CH}_2:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \xrightarrow{+\text{C}_2\text{H}_2} \text{C}_{10}\text{H}_7\cdot\text{NH}_2$ . Carbazole is probably attributable to intermediate diphenylamine. It is uncertain whether carbon dioxide acts merely as a diluent or takes part in the change in accordance with the equation



other gases, such as ammonia, hydrogen, nitrogen, or water vapour, give less satisfactory results. H. W.

**Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. IV. Quinoline Bases.** JULIUS VON BRAUN, ADOLF PETZOLD, and JON SEEMANN (*Ber.*, 1922, 55, [B], 3779–3792).—Under the conditions used by the authors, quinoline is readily and quantitatively hydrogenated at 210–215° into 1:2:3:4-tetrahydroquinoline, which can thus be prepared more readily than by the older methods. At 250°, a portion of the tetrahydro-base is reduced further to decahydroquinoline, and another portion is reduced to tertiary bases of pyridine character which have not been fully examined. Quinoline derivatives which contain a substituent in the benzenoid nucleus or in position 1 behave in the same manner as the parent bases, whereas those which have a substituent in position 3 are also hydrogenated in the benzenoid nucleus to an extent which depends on the particular substituent present.

The reductions are effected with the pure bases or with solutions of them in tetra- or deca-hydronaphthalene. The results are similar in every case, and the rate of absorption of the gas is not appreciably influenced by the diluent.

6-Methylquinoline is converted at 120° into 6-methyl-1:2:3:4-tetrahydroquinoline, b. p. 131–133°/9 mm., m. p. 37–38°, the yield being 90% of that theoretically possible. 6-Chloro-1:2:3:4-tetrahydroquinoline, long, colourless needles, m. p. 43°, b. p. 155°/18 mm., is prepared at 160°; the corresponding hydrochloride, m. p. 190°, picrate, yellow needles, m. p. 150°, and nitroso-derivative, yellow, lustrous prisms, m. p. 67°, are described.

[With A. SCHULTHEISS.]—6:7-Ethylenedioxyquinoline (Sonn and Benirschke, A., 1921, i, 805) is very readily hydrogenated at 180–190° to 6:7-ethylenedioxy-1:2:3:4-tetrahydroquinoline,

b. p.  $193^{\circ}/11$  mm., m. p.  $101^{\circ}$  (*picrate*, m. p.  $168^{\circ}$ ; hydrochloride, m. p.  $199^{\circ}$  (Sonn and Benirschke give m. p.  $201^{\circ}$ ); nitroso-derivative, m. p.  $110^{\circ}$ ).

2-Phenyl-1:2:3:4-tetrahydroquinoline, b. p.  $196-197^{\circ}/12$  mm., obtained from 2-phenylquinoline at  $150^{\circ}$ .

3-Ethylquinoline, an almost colourless liquid with an odour of quinoline, is prepared in 80% yield by the action of *n*-butyraldehyde on *o*-aminobenzaldehyde at  $120-130^{\circ}$  (cf. Wislicenus and Elvert, A., 1909, i, 420); it has b. p.  $135-138^{\circ}/12$  mm.,  $d_4^{20}$  1.0508,  $n_D^{20}$  1.6030 (hydrochloride, m. p.  $173^{\circ}$ ; *picrate*, m. p.  $197^{\circ}$ ; *methiodide*, m. p.  $191^{\circ}$ ). The base is readily hydrogenated at  $180-190^{\circ}$ , yielding thereby a mixture of 3-ethyl-5:6:7:8-tetrahydroquinoline and 3-ethyl-1:2:3:4-tetrahydroquinoline, which are separated from one another with the aid of benzoyl chloride. The former is a colourless liquid, b. p.  $125-128^{\circ}/12$  mm.,  $d_4^{20}$  0.99218,  $n_D^{20}$  1.5311; it gives a *methiodide*, m. p.  $120^{\circ}$ , and a *picrate*, yellow crystals, m. p.  $158^{\circ}$ . The latter has b. p.  $140^{\circ}/12$  mm.,  $d_4^{20}$  1.0041,  $n_D^{20}$  1.5625 (hydrochloride, m. p.  $210^{\circ}$ ; *picrate*, m. p.  $142^{\circ}$ ; *methiodide*,  $C_{18}H_{20}NI$ , m. p.  $205^{\circ}$ ; the benzoyl and nitroso-derivatives are non-crystalline).

3-*n*-Amylquinoline, prepared in almost quantitative yield from *o*-aminobenzaldehyde and heptaldehyde at  $180^{\circ}$ , is a colourless liquid, b. p.  $179^{\circ}/16$  mm.,  $d_4^{20}$  1.0048,  $n_D^{20}$  1.5715 (hydrochloride, m. p.  $174^{\circ}$ ; *picrate*, m. p.  $153^{\circ}$ ; *methiodide*, m. p.  $69^{\circ}$ ). It is hydrogenated at  $180-190^{\circ}$  with the formation of approximately equal amounts of 3-*n*-amyl-1:2:3:4-tetrahydroquinoline, a colourless liquid, b. p.  $159-164^{\circ}/12$  mm.,  $d_4^{20}$  0.96625,  $n_D^{20}$  1.5339 (hydrochloride, needles, m. p.  $124^{\circ}$ , *methiodide*,  $C_{16}H_{26}NI$ , m. p.  $145^{\circ}$ ; the *picrate*, benzoyl compound, acetyl derivative, and nitroso-compound are non-crystalline) and 3-*n*-amyl-5:6:7:8-tetrahydroquinoline, a colourless, nearly odourless liquid, b. p.  $167^{\circ}/12$  mm.,  $d_4^{20}$  0.96028,  $n_D^{20}$  1.5188. The latter substance gives a *picrate*, long needles, m. p.  $135^{\circ}$ , and a *methiodide*, m. p.  $105^{\circ}$ , whereas the chloride and chloroplatinate are non-crystalline; it does not react with acetic anhydride or nitrous acid. The base is oxidised by potassium permanganate to oxalic and pyridine-2:3:5-tricarboxylic acids.

3-Phenylquinoline is hydrogenated with remarkable ease at  $160^{\circ}$  to a mixture of 3-phenyl-1:2:3:4-tetrahydroquinoline and 3-phenyl-5:6:7:8-tetrahydroquinoline, from which the former is very readily separated by taking advantage of its sparing solubility in alcohol, with which the latter is readily miscible. 3-Phenyl-1:2:3:4-tetrahydroquinoline is a colourless, crystalline substance, m. p.  $83^{\circ}$  (hydrochloride, matted needles, m. p.  $229^{\circ}$ ; *picrate*, m. p.  $181^{\circ}$ ; *picrolonate*, a yellow powder, m. p.  $205^{\circ}$ ; acetyl derivative, feathery crystals, m. p.  $78^{\circ}$ ; nitroso-compound, m. p.  $147^{\circ}$ ). 3-Phenyl-5:6:7:8-tetrahydroquinoline is a colourless liquid, b. p.  $211-212^{\circ}/18$  mm. (hydrochloride, m. p.  $235^{\circ}$  after darkening at  $225-230^{\circ}$ ; *picrolonate*, a yellow powder, m. p.  $201^{\circ}$ ; *methiodide*,  $C_{18}H_{20}NI$ , m. p.  $240-243^{\circ}$ ; the base does not react with nitrous acid or acetic anhydride). 3-Phenyl-5:6:7:8-tetrahydro-

quinoline is reduced by sodium and ethyl alcohol to 3-phenyl-decahydroquinoline, colourless crystals, m. p. 98° after softening at 95° (nitroso-derivative, m. p. 110°; *picrate*, m. p. 210—212°; the acetyl compound could not be caused to crystallise). H. W.

**The Relative Stability of Cyclic Bases. VII. Substituted Tetrahydroquinoline Rings.** JULIUS VON BRAUN, JON SEE-MANN, and ADAM SCHULTHEISS (*Ber.*, 1922, 55, [B], 3803—3817).—In previous communications (von Braun and Neumann, A., 1917, i, 282; von Braun, Heider, and Neumann, A., 1917, i, 167), it has been pointed out that whereas the stability of the tetrahydroquinoline ring towards scission during reduction by sodium amalgam is little affected by the introduction of the methyl group in position 2, that of the dihydroindole ring is modified profoundly by 2 or 3 methylation. The presence of a methyl group in position 3 or 4 in the tetrahydroquinoline ring is now shown not to exert a marked effect on the course of the change. On the other hand, the presence of a phenyl group in position 2 causes the almost quantitative rupture of the non-aromatic ring linking, whereas when the group is in position 3 the three possible types of change are realised.

1:3-Dimethyl-1:2:3:4-tetrahydroquinoline,  $C_6H_4 \begin{smallmatrix} \text{CH}_2-\text{CHMe} \\ \text{NMe}-\text{CH}_2 \end{smallmatrix}$ ,

an almost colourless liquid, b. p. 130—132°/17 mm., is obtained by the reduction of 3-methylquinoline methiodide by tin and hydrochloric acid; the very hygroscopic *hydrochloride*, m. p. about 110°, *picrate*, m. p. 131°, and *methiodide*, m. p. 204°, are described. The corresponding quaternary *chloride* is converted by sodium amalgam into a mixture of 1:3-dimethyl-1:2:3:4-tetrahydroquinoline and  $\gamma$ -phenyl-3-methylpropyldimethylamine,

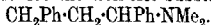


from which the former is removed by treatment with formaldehyde in hydrochloric acid solution. The latter base is a colourless liquid, b. p. 100—105°/7 mm., 221°/atmospheric pressure (*hydrochloride*, m. p. 90°; *picrate*, m. p. 87°; *methiodide*, m. p. 140°).

1:4-Dimethyl-1:2:3:4-tetrahydroquinoline *methiodide* is converted into the corresponding *chloride*, which is transformed by sodium amalgam into 1:4-dimethyl-1:2:3:4-tetrahydroquinoline and  $\gamma$ -phenylbutyldimethylamine,  $CHMePh-CH_2-CH_2-NMe_2$ , a liquid, b. p. 112—115°/7 mm. (*hydrochloride*, m. p. 100°; *picrate*, m. p. 98°; *methiodide*, m. p. 125°), which constitutes 60% of the mixture of bases.

2-Phenyl-1:2:3:4-tetrahydroquinoline is converted by methyl iodide and aqueous alkali mainly into 2-phenyl-1-methyl-1:2:3:4-tetrahydroquinoline, colourless crystals, m. p. 101°, b. p. 188—192°/14 mm.; the corresponding *hydrochloride*, m. p. 157°, *chloroplatinate*, m. p. 172°, *nitroso*-compound, a microscopic, green powder, m. p. 75°, and *diphenylmethane* derivative,  $C_{17}H_{19}N$ , m. p. 60° after slight previous softening, are described. The base unites with difficulty with methyl iodide to give the quaternary *iodide*,  $C_{17}H_{19}NI$ , m. p. 185°. The quaternary *chloride* (*chloro-*

platinate, orange-coloured crystals, m. p. 203°) is almost quantitatively converted by sodium amalgam into *o*- $\gamma$ -phenylpropyldimethylaniline,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , b. p. 175–178°/10 mm. The *picrate*, golden-yellow needles, m. p. 110°, the non-crystalline *hydrochloride*, and the *chloroplatinate*, a yellowish-brown powder, n. p. 170°, are described. The base does not unite readily with methyl iodide, thus proving that the dimethylamino-group is attached to the benzenoid nucleus and is sterically hindered, and that the compound is not the isomeric substance,

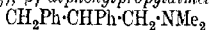


2-Phenyl-1-methyl-1:2:3:4-tetrahydroquinoline suffers fission in accordance with the scheme  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2-\text{CH}_2 \\ \text{NMe}\cdot\text{CHPh}\end{smallmatrix}\right\rangle + \text{BrCN} \rightarrow$

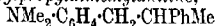
$\text{CN}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPhBr}$  to the extent of at least 50% when treated with cyanogen bromide in a gently boiling water-bath. Since cyanoamides cannot be distilled without decomposition and seldom crystallise, the product of the action is treated directly with an excess of piperidine, whereby it is converted into a portion insoluble in acid, b. p. 218°/vacuum, and a bromine-free, amorphous base which readily unites with methyl iodide, giving the substance  $\text{C}_{22}\text{H}_{20}\text{N}_3\text{I}$ , a pale-brown, microcrystalline powder which loses methyl iodide without definitely melting above 60°.

The *hydroxide*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2-\text{CH}_2 \\ \text{NMe}_2(\text{OH})\end{smallmatrix}\right\rangle\text{CHPh}$ , is mainly decomposed with loss of methyl alcohol when distilled under diminished pressure, giving 2-phenyl-1-methyl-1:2:3:4-tetrahydroquinoline.

In striking contrast to the 2-phenyl derivative, 3-phenyl-1:2:3:4-tetrahydroquinoline is readily converted by methyl iodide into the quaternary *iodide*,  $\text{C}_{17}\text{H}_{20}\text{NI}$ , m. p. 172°, which loses methyl iodide when distilled under diminished pressure and gives 3-phenyl-1-methyl-1:2:3:4-tetrahydroquinoline, m. p. 42°, b. p. 195–202°/12 mm. The corresponding *picrate*, m. p. 178°, the non-crystalline *hydrochloride*, and *chloroplatinate*, m. p. 192°, the *nitroso*-compound, m. p. about 105°, and the diphenylmethane derivative,  $\text{C}_{30}\text{H}_{24}\text{N}_2$ , m. p. 92°, are described. The quaternary *chloride* (*chloroplatinate*, m. p. 204°) is converted by sodium amalgam into a mixture of 3-phenyl-1-methyl-1:2:3:4-tetrahydroquinoline (47%),  $\beta$ -*phenylpropyldimethylamine*,



(45%), and *o*- $\beta$ -phenylpropyldimethylaniline,



(3%). The two bases last mentioned are separated by taking advantage of the inability of the *o*-dimethylaniline derivative to unite with methyl iodide in ethereal solution. The quantity of  $\beta$ -phenylpropyldimethylaniline available was insufficient to permit its isolation in a homogeneous condition, and it is characterised by its *picrate*, m. p. 166–167°, non-crystalline *hydrochloride*, and *chloroplatinate*, m. p. 181°.  $\beta$ -*Diphenylpropyldimethylamine* *methide* is exceedingly hygroscopic; it is converted into the corresponding *chloride* (*chloroaurate*, yellow needles, m. p. 164°; *chloroplatinate*, a microcrystalline powder, m. p. 236°). The constitution

of the iodide is established by the observation that the corresponding *hydroxide* is decomposed when distilled under diminished pressure into  $\alpha$ -benzylstyrene,  $\text{CH}_2\text{Ph}\cdot\text{CPh}\cdot\text{CH}_2$ , a liquid, b. p.  $140-148^\circ/\text{vacuum}$ ,  $d_4^{20} 1.0143$ ,  $n_D^{20} 1.5903$  (corresponding *dibromide*, colorless crystals, m. p.  $98^\circ$ ). 3-Phenyl-1-methyl-1:2:3:4-tetrahydroquinoline is converted to a slight extent by cyanogen bromide into the corresponding *methobromide* (identified by its conversion into the chloroplatinate, m. p.  $203^\circ$ ) but mainly into 1-cyano-3-phenyl-1:2:3:4-tetrahydroquinoline, m. p.  $78^\circ$ ; fission of the ring, as in the case of the 2-phenyl compound, is not observed.

6:7-Ethylenedioxyquinoline methiodide, m. p. 270°, is reduced by tin and hydrochloric acid to 6:7-ethylenedioxy-1-methyl-1:2:3:4-tetrahydroquinoline, colourless leaflets, m. p. 53°, b. p. 165–170°/8 mm.; the hydrochloride, m. p. 203°, picrate, m. p. 170°, and the methiodide, m. p. 220°, are described. The latter compound is prepared more advantageously by exhaustive methylation of 6:7-ethylenedioxy-1:2:3:4-tetrahydroquinoline. It is converted into the corresponding chloride which is transformed by sodium amalgam into a mixture of 6:7-ethylenedioxy-1-methyl-1:2:3:4-tetrahydroquinoline (40%) and  $\gamma$ -3:4-ethylenedioxy-phenylpropyldimethylamine,  $C_2H_5O_2C_3H_7[CH_2]_3NMe_2$ , b. p. 162–164°/7 mm., which are separated from one another by careful fractional distillation; the methiodide, m. p. 165°, picrate, m. p. 167°, and hydrochloride, m. p. 169°, of the latter base are described. H. W.

**The Mechanism of Syntheses of isoQuinoline from Benzylamine Derivatives.** PAUL STAUB (*Helv. Chim. Acta*, 1922, 5, 889-894).—Many attempts to synthesise isoquinoline derivatives by ring closure in appropriate benzylamine derivatives are recorded in the literature, but few were successful. In an attempt to determine the conditions requisite for success, the following new compounds were prepared for ring closure experiments.

$\alpha$ -Benzylideneaminoisopropyl alcohol,  $\text{CHPh:N-CH}_2\text{-CHMe-OH}$ , was obtained by reducing nitroisopropyl alcohol,

and condensing the product with benzaldehyde; it crystallises in needles, m. p. 76–76.5°.

Benzylaminoisopropyl alcohol,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ , was obtained by the action of benzyl chloride on aminoisopropyl alcohol; b. p.  $142^\circ/11$  mm.

*Benzenesulphonbenzyl-β-hydroxyethylamide*,

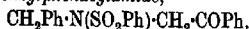
$$\text{CH}_2\text{Ph}\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH},$$

was prepared by heating benzenesulphonbenzylamide with ethylene oxide at 170°; it formed a viscous liquid crystallising slowly, and was not purified.

*Benzenesulphonbenzyl-β-bromoethylamide,*

$$\text{CH}_2\text{Ph}\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CH}_2\text{Br},$$

was formed by the action of ethylene bromide on sodium benzene-sulphonbenzylamide in ether; m. p. 82.5–83°.

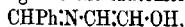
*Benzenesulphonbenzylphenacylamide,*

was prepared by the action of bromoacetophenone on sodium benzenesulphonbenzylamide in ether. The product was not crystallised.

*Acetobenzylphenacylamide*,  $\text{CH}_2\text{Ph}\cdot\text{N}(\text{Ac})\cdot\text{CH}_2\cdot\text{COPh}$ , was obtained as a syrup from the action of bromoacetophenone on sodium benzylacetamide.

In no case could any *isoquinoline* derivative be obtained by the action of any of the usual ring-closing agents on any of the above six compounds.

It is concluded that a benzene derivative containing the chain  $\text{Ph}\cdot\text{C}\cdot\text{N}\cdot\text{C}\cdot\text{C}-$  must, if it is to be convertible into an *isoquinoline* base, conform to two rules. In the lateral chain it must have (1) a system of conjugated double bonds, actual or potential; (2) a hydroxyl or alkoxyl group in  $\beta$ -position to the nitrogen atom. The compound  $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$  conforms to condition (1) by loss of alcohol, and readily forms *isoquinoline*. Benzylaminoacetaldehyde,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHO}$ , which is converted by fuming sulphuric acid into *isoquinoline*, may be supposed to undergo oxidation and by passing into the tautomeric form,



satisfies the conditions.

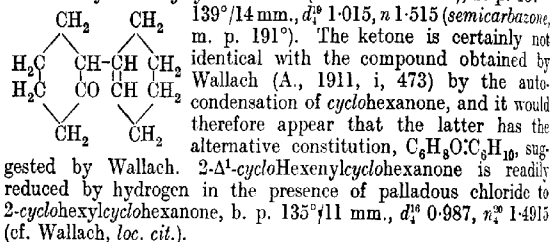
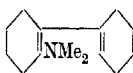
E. H. R.

**Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. V. The Carbazole Complex.** JULIUS VON BRAUN and HEINRICH RITTER (*Ber.*, 1922, 55, [B], 3792—3803; cf. Padoa and Chiaves, A., 1908, i, 772).—The process used by the authors does not cause the hydrogenation of pyrazole even at 260° and under a pressure of 30 atmospheres, in spite of the use of a material which has been exhaustively purified in several different manners. Nevertheless, the authors are inclined to the view that pure pyrazole is not unusually resistant to hydrogenation, and that the failure of their experiments is due to some unknown catalytic impurity. The *N*-alkylcarbazoles are readily hydrogenated with initial addition of four hydrogen atoms to one benzene nucleus. Subsequently, the second benzene nucleus is attacked with addition of a further four atoms of hydrogen.

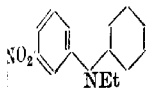
9-Methylcarbazole readily absorbs about seven atomic proportions of hydrogen at 210—215° and 25 atmospheres pressure. About 40% of the initial material remains unchanged whilst a portion is perhydrogenated with production of ammonia. The liquid product of the reaction is a mixture of the octahydro- and tetrahydro-derivatives with 9-methylcarbazole, from which the first-named is readily separated by treatment with hydrochloric acid (20%), in which it alone dissolves. The remaining bases cannot be separated from one another by distillation or crystallisation; the presence of the tetrahydro-compound is established by the formation of the strongly basic hexahydro-derivative when the mixture of bases is treated with tin and hydrochloric acid.

9-Methyloctahydrocarbazole,  $\text{MeN} \begin{smallmatrix} \text{C}_6\text{H}_8 \\ \text{C}_6\text{H}_8 \end{smallmatrix}$ , lustrous leaflets, m. p. 94°, b. p. 176–178°/16 mm., is somewhat unstable towards air and does not give the pine-shaving or the dimethylaminobenzaldehyde reaction. It does not give a well-defined picrate or methiodide; it is readily oxidised by chromic acid, potassium permanganate, or ferric chloride, but it has not yet been found possible to isolate uniform products of the action. It is conveniently reduced by tin and boiling hydrochloric acid (20%) to 9-methyldecahydrocarbazole,  $\text{MeN} \begin{smallmatrix} \text{C}_8\text{H}_{10} \\ \text{C}_8\text{H}_{10} \end{smallmatrix}$ , a colourless, mobile liquid, b. p.

138–139°/12 mm., which is stable towards air; the non-crystalline hydrochloride, hydrobromide, m. p. 202–204°, picrate, m. p. 162°, and methiodide, m. p. 189°, are described. The presence of the double bond in the base is betrayed only by its instability towards permanganate; it yields only the hydrobromide when treated with fuming hydrobromic acid and does not unite with bromine or hydrogen even under widely varied conditions. The methiodide is transformed by successive treatment with silver oxide and distillation into 2-dimethylamino- $\Delta^{1:1'}$ -dicyclohexenyl (annexed formula), an almost colourless liquid, b. p. 148°/15 mm., which is conveniently characterised as the picrate, m. p. 157°. The new base is somewhat unstable and is readily converted by sulphuric acid (10%) into 2- $\Delta^1$ -cyclohexenylcyclohexanone (annexed formula), b. p. 131–139°/14 mm.,  $d_4^{20}$  1.015,  $n_D^{20}$  1.515 (semicarbazone, m. p. 191°). The ketone is certainly not identical with the compound obtained by Wallach (A., 1911, i, 473) by the autocondensation of cyclohexanone, and it would therefore appear that the latter has the alternative constitution,  $\text{C}_6\text{H}_8\text{O} \cdot \text{C}_6\text{H}_{10}$ , suggested by Wallach. 2- $\Delta^1$ -cyclohexenylcyclohexanone is readily reduced by hydrogen in the presence of palladium chloride to 2-cyclohexylcyclohexanone, b. p. 135°/11 mm.,  $d_4^{20}$  0.987,  $n_D^{20}$  1.4915 (cf. Wallach, loc. cit.).



The reduction of 9-ethylcarbazole is very similar to that of the methyl compound. 9-Ethylcarbazole, lustrous leaflets, m. p. 43°, b. p. 162–163°/9 mm., is unstable towards air; it does not give a methiodide or a picrate. It is readily reduced to 9-ethyldecahydrocarbazole, a colourless liquid which is stable towards air, b. p. 140–141°/12 mm.; the non-crystalline hydrochloride, the picrate, m. p. 133°, and the methiodide, m. p. 176–177°, are described. 2-Methylethylamino- $\Delta^{1:1'}$ -dicyclohexenyl is a colourless liquid, b. p. 148–150°/12 mm., which gives a non-crystalline picrate and methiodide. It is readily transformed by dilute sulphuric acid into 2- $\Delta^1$ -cyclohexenylcyclohexanone and methyl-ethylamine. 9-Ethylhexahydrocarbazole is a colourless, odourless liquid, b. p. 155–157°/8 mm., 292–293°/749 mm.; it gives a well-defined methiodide, m. p. 174°. The base is transformed by a mixture of nitric and sulphuric acids at 0° into the nitro-com-



compound (annexed formula), golden-yellow needles, m. p.  $142^{\circ}$ , which is reduced by stannous chloride to 7-amino-9-ethylhexahydrocarbazole, an almost colourless, very viscous liquid, b. p.  $224-225^{\circ}/24$  mm., which shows all the colour reactions

characteristic of the simpler meta-diamines of the aromatic series.

It has not been found possible to effect the smooth dehydrogenation of 9-methyl- or 9-ethyl-hexahydrocarbazole; if the substances are passed over lead oxide and pumice the alkyl residues are lost and carbazole is produced.

H. W.

**Benzo-polymethylene Compounds. VIII. Cyclic Analogues of Atophan.** JULIUS VON BRAUN and PAUL WOLFF (*Ber.*, 1922, 55, [B], 3675-3688).—1-Ketotetrahydronaphthalene condenses

readily with isatin to give 5:6-dihydro- $\alpha$ -naphthacridine-7-carboxylic acid (annexed formula), which readily undergoes further change. Constitutionally the new compound (for

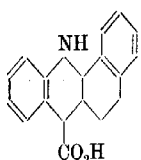
which the name tetraphan is proposed) is allied somewhat closely to 2-phenyl-4-cinchoninic acid (atophan), from which, however, it differs entirely in its physiological action, having a characteristic effect on the spinal marrow somewhat resembling that of strychnine. The physiological properties

of a number of its derivatives have been examined. Substitution in the benzenoid nuclei of the isatin and tetrahydronaphthalene complexes does not affect the qualitative nature of the action. The presence of the basic nitrogen atom and of the carboxyl group appears essential. A new ring produced by the insertion of more than one carbon atom into the atophan complex must be present, which must not be eccentrically united. The group  $-\text{CH}_2\text{CH}_2-$  need not be so fully hydrogenated.

Since tetrahydroatophan shows close physiological resemblance to tetraphan, it is to be expected that the action of the latter would be considerably enhanced by transforming it into its tetrahydro-derivative; the reverse is, however, found to be the case.

5:6-Dihydro- $\alpha$ -naphthacridine-7-carboxylic acid, slender, pale yellow needles, m. p.  $252^{\circ}$  (decomp.), is prepared smoothly by heating a mixture of isatin and 1-ketotetrahydronaphthalene with aqueous-alcoholic potassium hydroxide solution. It reacts incompletely with mineral acids, yielding salts which are hydrolysed by water. The sodium, lead, basic copper, and silver salts are described; the ethyl ester, long, coarse needles, m. p.  $80^{\circ}$ , is prepared from the latter. The acid is decomposed when heated somewhat above its melting point into 5:6-dihydro- $\alpha$ -naphthacridine, b. p.  $237-238^{\circ}/10$  mm., m. p.  $60^{\circ}$ ; the corresponding hydrochloride, long needles, m. p.  $226^{\circ}$ , picrate, m. p.  $206^{\circ}$ , and methiodide, a reddish-yellow, crystalline powder, decomp.  $191^{\circ}$ , are described. The base is readily dehydrogenated by lead oxide at  $300-320^{\circ}$  with production of  $\alpha$ -naphthacridine, m. p.  $108^{\circ}$ . It is oxidised by chromic acid in glacial acetic acid solution to 5:6-diketo- $\alpha$ -naphthacridine, an orange-coloured powder, m. p.  $242^{\circ}$  (a salt with chromic acid is described).

5:6-Dihydro- $\alpha$ -naphthacridine-7-carboxylic acid is converted by bromine and glacial acetic acid at 120–130° into  $\alpha$ -naphthacridine-7-carboxylic acid, a yellow powder, m. p. 261°; the cobalt, copper, mercuric, and silver salts are described. The methyl ester has m. p. 83°. When heated above its melting point, the acid is converted into  $\alpha$ -naphthacridine, m. p. 108°.

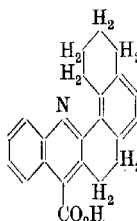


5:6-Dihydro- $\alpha$ -naphthacridine-7-carboxylic acid is reduced by sodium and ethyl or amyl alcohol to 5:6:6a:7:12:12a-hexahydro- $\alpha$ -naphthacridine-7-carboxylic acid (tetrahydrotetrophan) (annexed formula), m. p. 190° (decomp.) after softening at 180°; the corresponding nitroso-compound, m. p. 149°, and acetyl derivative, m. p. 247° after softening at 244°, are described.

5:6-Dihydro-11-methyl- $\alpha$ -naphthacridine-7-carboxylic acid, colourless crystals, m. p. 188° (decomp.), is prepared from 1-ketotetrahydronaphthalene and *o*-methylisatin; its metallic salts closely resemble those of the parent acid. 5:6-Dihydro-11-methyl- $\alpha$ -naphthacridine has m. p. 93–94°, b. p. 248–253°/16 mm.; it yields a picrate, m. p. 141°, and a hydrochloride, long, pale yellow needles, m. p. 173°, but could not be caused to react with methyl iodide. 11-Methyl- $\alpha$ -naphthacridine, m. p. 107°, gives a picrate, m. p. 155°, and a hydrochloride, m. p. 136°, but does not react with methyl iodide.

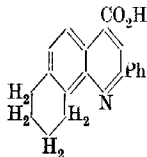
5:6-Dihydro-9-methyl- $\alpha$ -naphthacridine-7-carboxylic acid has m. p. 293° (decomp.); the sodium salt dissolves very sparingly in water.

9-Chloro-5:6-dihydro- $\alpha$ -naphthacridine-7-carboxylic acid, m. p. 283° (decomp.), is converted when heated above its melting point into 9-chloro-5:6-dihydro- $\alpha$ -naphthacridine, m. p. 102°, b. p. 257–262°/14 mm. The hydrochloride of the latter has m. p. 240°. The base loses the chlorine atom when it is treated with lead oxide.



9-Bromo-5:6-dihydro- $\alpha$ -naphthacridine-7-carboxylic acid has m. p. 265°; the silver salt and the methyl ester, yellow leaflets, m. p. 128°, are described. 9-Bromo-5:6-dihydro- $\alpha$ -naphthacridine crystallises in pale yellow needles, m. p. 168° (hydrochloride, m. p. 211–212°).

5:6-Dihydro-1:2-tetramethylene- $\alpha$ -naphthacridine-7-carboxylic acid (annexed formula) is prepared from isatin and  $\alpha$ -keto-octahydrophenanthrene; it has m. p. 210° (decomp.) after darkening at 180°.



2-Acenaphthylquinoline-4-carboxylic acid, prepared from 4-acetylacenaphthene and isatin, has m. p. 234° after previous softening.

Tetramethylenetophan (annexed formula), prepared from *ar*- $\alpha$ -aminotetrahydronaphthylamine, pyruvic acid, and benzaldehyde, forms yellow crystals, m. p. 260° after softening at 255°; its physiological action resembles that of atophan.

H. W.

**The Relationship between Fluorescence and Chemical Constitution in the Case of Derivatives of Benzoxazole. II.**

F. HENRICH [with H. SUNTHEIMER and C. STEINMANN] (*Ber.*, 1922, **55**, [B], 3911—3921).—In a previous communication (*A.*, 1921, i, 886), it has been shown that the development of fluorescence in alkaline solutions of hydroxybenzoxazole derivatives,

$\text{HO}\cdot\text{C}_6\text{H}_3\text{<}\overset{\text{N}}{\text{O}}\text{>C}\cdot\text{R}(\mu)$ , is observed only when R in position  $\mu$  is

an aromatic nucleus directly attached by one of its carbon atoms to the  $\mu$  carbon atom and when the hydroxyl group is in the para-position to the nitrogen atom. This regularity is now shown to be true of certain derivatives of 2:4-dihydroxytoluene.

2:4-Dihydroxytoluene, m. p. 105—107°, is prepared from 2:4-diaminotoluene through the compounds 2-amino-4-acetamidotoluene, 4-acetamido-2-hydroxytoluene, and 4-amino-2-hydroxytoluene; the necessary conditions for each change are described fully in the original. It is converted by amyl nitrite and potassium hydroxide in absolute alcoholic solution into 5-nitroso-2:4-dihydroxytoluene, decomp. 175—180° according to the rate of heating after darkening and softening at 146°; the potassium salt and the benzoyl derivative, m. p. 146—153°, are described.

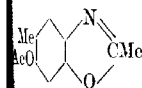
2:4-Dihydroxytoluene is converted by fuming nitric acid in the presence of ether into a mixture of 3-nitro-2:4-dihydroxytoluene, bright red needles, m. p. 111°, and 5-nitro-2:4-dihydroxytoluene, orange-yellow needles, m. p. 118—119°, which can be separated from one another by taking advantage of the volatility of the former with steam, with which the latter does not volatilise.

5-Amino-2:4-dihydroxytoluene hydrochloride, long, colourless needles, is prepared by the reduction of the corresponding nitroso- or nitro-compound with stannous chloride and concentrated hydrochloric acid. The free amine is obtained by the addition of sodium hydroxide to an aqueous solution of the hydrochloride; it dissolves to a dark blue solution in an excess of the reagent, and readily absorbs oxygen, without, however, becoming converted into dyes of the type of litmus. The hydrochloride is transformed by acetic anhydride into 6-acetoxy-2-methyl-5-methylbenzoxazole (anhydrous formula), colourless needles, m. p. 94°, which is converted

by alcoholic potassium hydroxide solution into 6-hydroxy-2:5-dimethylbenzoxazole, colourless crystals, m. p. 221°; the latter substance does not fluoresce in aqueous alkaline solution.

6-Benzoyl-2-phenyl-5-methylbenzoxazole, colourless crystals, m. p. 164—165° after softening at 163°, is prepared from 5-amino-2:4-dihydroxytoluene hydrochloride and benzoyl chloride and is hydrolysed by alcoholic potassium hydroxide solution to 6-hydroxy-2-phenyl-5-methylbenzoxazole, colourless crystals, m. p. 242° after softening at 236°, which has a green fluorescence in aqueous sodium hydroxide solution.

3-Nitro-2:4-dihydroxytoluene is reduced by stannous chloride and concentrated hydrochloric acid to 3-amino-2:4-dihydroxytoluene hydrochloride, colourless needles, which is converted by



successive treatment with benzoyl chloride and alcoholic potassium hydroxide solution into 4-hydroxy-2-phenyl-5-methylbenzoxazole, colourless crystals which do not exhibit fluorescence in alkaline solution. H. W.

**The Relative Stability of Cyclic Bases. VIII. The Phenmorpholine and Homotetrahydroquinoline Rings.** JULIUS VON BRAUN and JON SEEMANN (*Ber.*, 1922, 55, [B], 3818—3825).—It is shown that the stability of the morpholine ring is increased to an unexpected extent by its association with an aromatic ring, so that it is at least as stable towards cyanogen bromide as 1 : 2 : 3 : 4-tetrahydroquinoline and even more stable towards sodium amalgam. Homo-1 : 2 : 3 : 4-tetrahydroquinoline does not suffer fission under the action of cyanogen bromide.

The nine rings (pyrrolidine, piperidine, morpholine, dihydroindole, dihydroisoindole, 1 : 2 : 3 : 4-tetrahydroquinoline, 1 : 2 : 3 : 4-tetrahydroisoquinoline, phenmorpholine, and homo-1 : 2 : 3 : 4-tetrahydroquinoline) exhibit uniformity in their behaviour towards cyanogen bromide, sodium amalgam, and the Hofmann degradation if the dihydroindole and the phenmorpholine systems are not considered. The peculiarity of the latter rings appears to be caused by the presence in them of the group  $-\text{Ar}-\text{N}-\text{CH}_2-\text{CH}_2-$ .

N- $\beta$ -Hydroxyethyl-o-anisidine is conveniently prepared in 75–80% yield by heating o-anisidine with a considerable excess of ethylene chlorohydrin on a water-bath; the *picrate*, m. p. 140°, and the *hydrochloride*, m. p. 134°, are described. The base is converted by successive treatment with concentrated hydrochloric acid at 160–180° and with dilute aqueous alkali into phenmorpholine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CH}_2 \end{smallmatrix}$ , b. p. 127–128°/12 mm. The latter is

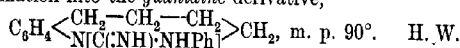
transformed quantitatively by methyl iodide and sodium hydroxide into 1-methylphenmorpholinium methiodide, which is decomposed when distilled under diminished pressure into 1-methylphenmorpholine, b. p. 124°/12.5 mm. (*picrate*, m. p. 144°).

1-Methylphenmorpholine reacts slowly with cyanogen bromide at the temperature of boiling water, giving unchanged material; 4-methylphenmorpholine *methobromide*, m. p. 213°, and 4-cyano-phenmorpholine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CH}_2 \\ | \\ \text{N}(\text{CN})\cdot\text{CH}_2 \end{smallmatrix}$ , a liquid, b. p. 115–118°/1 mm.;

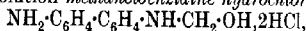
the latter could not be obtained in a perfectly homogeneous condition, and is characterised by converting it into the guanidine derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CH}_2 \\ | \\ \text{N}[\text{C}(\text{NH})\cdot\text{NHPh}]\cdot\text{CH}_2 \end{smallmatrix}$ , small, colourless needles,

m. p. 152°, the non-crystalline *hydrochloride* and *chloroplatinate*, m. p. 144°, of which are described. 4-Methylphenmorpholine methochloride is converted by sodium amalgam almost entirely into 4-methylphenmorpholine which is characterised by its conversion into the *diphenylmethane* derivative,  $\text{C}_{10}\text{H}_{22}\text{O}_2\text{N}_2$ , a very viscous liquid, b. p. about 260°/2 mm. (decomposition occurs before completion of the distillation) (*dimethiodide*, m. p. 157°).

The difficulty of methylating homo-1:2:3:4-tetrahydroquinoline,  $C_6H_4 \begin{smallmatrix} CH_2-CH_2 \\ NH-CH_2 \end{smallmatrix} > CH_2$ , has been indicated previously (von Braun and Bartsch, A., 1913, i, 197); it has now been found possible to isolate the products of the action in a homogeneous form. The quaternary iodide,  $C_{12}H_{18}NI$ , has m. p.  $155^\circ$ . 1-Methylhomo-1:2:3:4-tetrahydroquinoline has b. p.  $108-110^\circ/10$  mm., and gives a picrate, m. p.  $139^\circ$ , a non-crystalline hydrochloride, and a chloroplatinate, m. p.  $186^\circ$ ; it combines very slowly with methyl iodide. It is obtained as the sole basic product when the corresponding quaternary hydroxide is distilled in a vacuum. It is converted by cyanogen bromide into 1-methylhomo-1:2:3:4-tetrahydroquinoline methobromide (identified as the corresponding chloroplatinate, m. p.  $197^\circ$ ) and 1-cyanohomo-1:2:3:4-tetrahydroquinoline,  $C_6H_4 \begin{smallmatrix} [CH_2]_4 \\ N(CN) \end{smallmatrix} >$ , b. p.  $178-182^\circ/13$  mm., which could not be obtained completely free from bromine and is identified by transformation into the guanidine derivative,



**Condensation of Benzidine with Formaldehyde.** HEISA-  
SURO KONDO and SUEZO ISHIDA (*J. Pharm. Soc. Japan*, 1922, 79—985; cf. H. Schiff, A., 1892, 1223).—By adding 30 c.c. of 35% formaldehyde solution to benzidine (10 g.) dissolved in absolute alcohol (200 c.c.), a greyish-white, light, amorphous condensation product, dimethanolbenzidine,  $C_{12}H_8(NH-CH_2OH)_2$ , is precipitated; it has m. p.  $271-272^\circ$  after sintering at  $260^\circ$ , and is sparingly soluble in alcohol or water, but readily soluble in hydrochloric acid. It is not identical with dimethylenebenzidine, m. p.  $140-141^\circ$ , obtained by Schiff by the same method. When dissolved in dilute hydrochloric acid, the odour of formaldehyde is perceptible and from the solution methanolbenzidine hydrochloride,



colourless needles, of high melting point, was isolated by adding concentrated hydrochloric acid. When kept for a long time the solution in hydrochloric acid gave a reddish-violet product identical with the compound,  $C_{15}H_{12}N_2$ , obtained by Schiff. K. K.

**The Behaviour of certain Dibenzamidoethylene Derivatives Prepared from Iminazoles towards Acid Anhydrides. A.**

WINDAUS and W. LANGENBECK (*Ber.*, 1922, 55, [B], 3706—3709; cf. Windaus, Dörries, and Jensen, A., 1922, i, 61).—Dibenzamidoethylene derivatives are converted by the anhydrides of fatty acids into glyoxalines which contain the alkyl group of the fatty acid in position 2.

$\alpha^3$ -Dibenzamido- $\Delta^2$ -propylene is converted by acetic anhydride at  $180^\circ$  into 2:4(2:5)-dimethylglyoxaline, identified as the picrate, m. p.  $142^\circ$ . The action of propionic anhydride under similar conditions leads to the formation of 4(5)-methyl-2-ethylglyoxaline, hygroscopic crystals, m. p.  $45^\circ$  (oxalate, colourless leaflets, m. p.

145°; *picrate*, yellow prisms, m. p. 131°; *hydrochloride*, hygroscopic leaflets, m. p. 132°; *nitrate*, m. p. 129°).

4(5)-Ethylglyoxaline (cf. Kolshorn, A., 1904, i, 675) is converted by benzoyl chloride and sodium hydroxide into  $\alpha\beta$ -*dibenzamido*- $\Delta^a$ -*butylene*,  $\text{NHBz}\cdot\text{CH}\cdot\text{C}(\text{Et})\cdot\text{NHBz}$ , needles, m. p. 146°, which is transformed by acetic anhydride at 140° into 2-methyl-4(5)-ethylglyoxaline (*picrate*, yellow needles, m. p. 90–91°; *oxalate*, m. p. 141°).

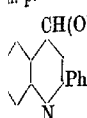
The glyoxaline obtained by Windaus and Ullrich (A., 1914, i, 662) by the action of ammonia on rhamnose is identified as 4(5)-methyl-5(4)-ethylglyoxaline. H. W.

**Preparation of Triarylmethane Dyestuffs.** BRITISH DYE STUFFS CORPORATION, LTD., JAMES BADDILEY, and ERNEST HARRY RODD (Brit. Pat. 189295).—New dyes of the triarylmethane series are obtained by condensing a 4 : 4'-dialkyldiamino-3 : 3'-dimethylbenzophenone with a suitable secondary or tertiary amine by warming with phosphoryl chloride with the addition of a neutral diluent if desired. These new basic products dye cotton mordanted with tannin-antimony valuable shades of bright reddish- to bluish-violet. Those containing phenyl, benzyl, or naphthyl residues substituted in the amino-groups can be sulphonated by warming with 20% fuming sulphuric acid, giving new acid dyes which dye wool level shades of violet. The ketones required for the synthesis may be obtained by boiling the corresponding thio-ketones with concentrated hydrochloric acid, and the latter are produced by the condensation of monoalkyl-*o*-toluidines with formaldehyde and converting the resulting diphenylmethane derivatives into thio-ketones by the process of Brit. Pat. 20615/14. 4 : 4'-*Diethyldiamino*-3 : 3'-*dimethylbenzophenone*, m. p. 165°, when condensed with ethyl-*o*-toluidine, gives the triphenylmethane dye in the form of a bronze-coloured paste which dyes mordanted cotton a reddish-violet. Bluer shades are obtained by condensing the ketone with benzylethylaniline or dibenzylaniline. G. F. M.

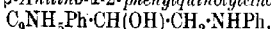
**Preparation of Aminopyridines.** CHEMISCHE FABRIK AUF ACTIEN (VOERM. E. SCHERING) (D.R.-P. 358397; from *Chem. Zentr.*, 1922, iv, 950).—Ammonia is allowed to act on pyridine or its homologues in the presence of alkali metals. For example, anhydrous pyridine at 80° is added to a suspension of finely divided sodium in toluene and anhydrous ammonia is passed in. After the sodium is used up the temperature is raised to 130° and so maintained until no more ammonia is absorbed. From the products of the reaction, by extracting with ether, distilling off the ether and fractionation of the residue, 2-*aminopyridine*, b. p. 103–110°/20 mm., 4 : 4'-*dipyridyl*, b. p. 173–180°/20 mm., and 4-*aminopyridine* are obtained. 6-*Amino*-2-*methylpyridine*, a yellow oil, b. p. 120–130°/20 mm., is similarly prepared from 2-methylpyridine ( $\alpha$ -picoline). G. W. R.

**Preparation of Amino-alcohols of the Quinoline Series.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 92001, 92607, 92608, and 92609; from *Chem. Zentr.*, 1922, iv, 950–951).—2-Phenyl-4-quinolyl methyl ketone is halogenated on the

methyl group and the halogen derivative allowed to react with primary or secondary amines. The *N*-alkyl-2-phenylquinolyl 4-aminomethyl ketone thus formed is reduced to the amino-alcohol. *Phenyl-4-quinolyl methyl ketone*, yellow crystals, m. p. 75°, is prepared by condensation of ethyl 2-phenylquinoline-4-carboxylate with ethyl acetate and elimination of carbon dioxide from the intermediate *ethyl 2-phenylquinoline-4-acetate*, m. p. 52–54°, or from *cyano-2-phenylquinoline* by Grignard's reaction. By the action of bromine on the ketone, *2-phenyl-4-quinolyl bromomethyl ketone hydrobromide* is obtained; it forms yellow crystals, m. p. about 25° (decomp.). The free *bromomethyl ketone* forms light yellow crystals, m. p. 91°. With dimethylamine it gives *2-phenyl-4-quinolyl 4-dimethylaminomethyl ketone*, which forms a *hydrochloride*, light yellow crystals, m. p. 208° (decomp.), and a *hydrobromide*, m. p. about 206°. Reduction of this compound gives  $\beta$ -dimethyl-



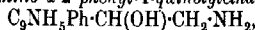
$\text{CH(OH)CH}_2\text{NMe}_2$  formula, a white, plastic mass. The *dihydrochloride* forms crystals, m. p. 175° (decomp.). *2-Phenyl-4-quinolyl diethylaminomethyl ketone* is similarly prepared; the *hydrobromide* forms yellow, felted needles, m. p. about 188° (decomp.). *2-Phenyl-4-quinolyl piperidinomethyl ketone* gives a *hydrochloride*, m. p. 235°, and a *hydrobromide*, m. p. about 241° (decomp.). *2-Phenyl-4-quinolyl dimethylaminomethyl ketone* forms yellow crystals, m. p. 123–125°. These ketones may be reduced to the corresponding amino-alcohols. *N*-Dimethylamino- $\alpha$ -2-phenyl-4-quinolyethanol gives a *dihydrochloride* which forms crystals, m. p. about 185°, with darkening.  $\beta$ -Piperidino- $\alpha$ -2-phenyl-4-quinolyethanol gives a *dihydrochloride*, m. p. about 99° (decomp.).  $\beta$ -Anilino- $\alpha$ -2-phenylquinolyethanol,



has m. p. 146°.

G. W. R.

**Preparation of a Primary Amino-alcohol of the Quinoline Series.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 2301; from *Chem. Zentr.*, 1922, iv, 951; cf. preceding abstract).—*2-Phenyl-4-quinolyl methyl ketone* is changed into its oximinomethyl ketone and this is submitted to reduction. *2-Phenyl-4-quinolyl oximinomethyl ketone* forms yellow crystals, m. p. 182° (decomp.). By reduction,  $\beta$ -amino- $\alpha$ -2-phenyl-4-quinolyethanol,



is obtained. It forms a *dihydrochloride*, colourless crystals, m. p. about 190° after softening at about 145°.

G. W. R.

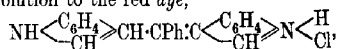
**Reduction of 4:4'-Dipyridyl.** OTTO DIMROTH and FRITZ FRISTER (*Ber.*, 1922, 55, [B], 3693–3697).—The formation of 1:1'-diacetyldihydro-4:4'-dipyridyl by the action of acetic anhydride on the dark violet solution obtained by the reduction of 4:4'-dipyridyl with nascent hydrogen, has been described previously (Dimroth and Frister, *A.*, 1922, i, 678). It is now shown that the violet solution contains a semiquinonoid compound

of molar proportions of 4:4'-dipyridyl and 1:1'-dihydro-4:4'-dipyridyl, which has been isolated as the dihydrochloride, for which the name dipyridyl-violet chloride is proposed. The dye differs from other semiquinonoid substances in that the reduced half is quinonoid and the oxidised half has the aromatic constitution. 4:4'-Dipyridyl is obtained conveniently and in 90—95% yield by the action of oxygen on a suspension of 1:1'-diacetyl-tetrahydro-4:4'-dipyridyl in glacial acetic acid and subsequent addition of sodium hydroxide to the solution. Titration of an aqueous solution of the substance with chromous chloride solution in the absence of air shows that the dye is produced by the action of one equivalent of hydrogen on a molecule of dipyridyl and that further reduction is not caused by chromous chloride. The dye is isolated as a dark green, crystalline powder,  $C_{20}H_{20}N_4Cl_2$ , by the action of chromous chloride on a solution of dipyridyl in the presence of calcium chloride; the precipitated product is washed successively with water and alcohol in the absence of air, towards which it is unusually sensitive.

H. W.

**Syntheses in the Indole Group. II. The Influence of the Solvent on the Grignard Reaction.** RIKO MAJIMA and MUNIO KOTAKE (*Ber.*, 1922, **55**, [B], 3865—3872).—The unexpected differences observed in the production of indole-3-aldehyde from magnesium indolyl iodide and formic ester according as the reaction is effected in the presence of aliphatic or arylaliphatic ethers (Majima and Kotake, this vol., i, 156) has led the authors to examine possible further cases of this kind. Better yields of the products of the action of magnesium indolyl iodide on carbon dioxide, acetone, or benzaldehyde are obtained in the presence of anisole than in that of ethyl ether, whereas the reverse is the case when ethyl chloroformate, acetyl chloride, or chloroacetyl chloride is used.

Indole-3-carboxylic acid, m. p. 218—220°, is obtained by the action of carbon dioxide on magnesium indolyl iodide in anisole or ethyl ether. The reaction has been examined previously by Oddo (*A.*, 1911, i, 486), who has thus isolated indole-1-carboxylic acid, m. p. 108°; the cause of the discrepancy has not been elucidated. Magnesium indolyl iodide and acetone give di-3-indolyl-dimethylmethane, m. p. 163—165° (cf. Scholtz, *A.*, 1913, i, 520). Di-3-indolylphenylmethane,  $CHPh(CH<\overset{C_6H_5}{CH}>NH)_2$ , m. p. 149—152° (+0.5C<sub>6</sub>H<sub>6</sub>), m. p. 120—121°, is prepared from magnesium indolyl iodide and benzaldehyde; it is oxidised by ferric chloride in alcoholic solution to the red dye,



m. p. about 245—248°. Ethyl chloroformate and magnesium indolyl iodide give ethyl indole-3-carboxylate, colourless crystals, m. p. 118—119°; Oddo's observation (*loc. cit.*) that ethyl indole-2-carboxylate, m. p. 107°, is produced could not be confirmed. Acetyl chloride and magnesium indolyl iodide yield 3-indolyl

methyl ketone,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{COMe}$ , m. p. 188—189° (oxime, m. p. 143—146°), identical with the products described by Oddo (*loc. cit.*). 3-Indolyl chloromethyl ketone forms small, rhombic crystals, m. p. 212—214°. H. W.

**Isomeric Relationships in the Pyrazole Series.** K. von AUWERS and H. BROCHE (*Ber.*, 1922, 55, [B], 3880—3911).—An examination has been made of the possibility of the existence of isomerides of the types  $\text{RN} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{N} = \text{CH} \end{smallmatrix}$  and  $\text{RN} \begin{smallmatrix} \text{N} - \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix}$ , in the pyrazole series analogous to those observed with the closely related indazoles,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{NR} \end{smallmatrix} \text{N}$  and  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} \text{NR}$ . The alkyl and

phenyl derivatives of 3-methyl- and 3:5-dimethyl-pyrazole have been investigated, but evidence of existence of isomerides of the expected type has not been obtained. The observations which have been made throw doubt on the identity of 3- and 5-derivatives of pyrazole as assumed by Knorr and other investigators.

3-Methylpyrazole is converted by an equivalent amount of methyl iodide in ethereal solution at 120° into 1:3-dimethylpyrazole (*picrate*, m. p. 172.5°; cf. Jowett and Potter, T., 1903, 83, 467), a portion of the base remaining, however, unchanged. The same substances are obtained by boiling 3-methylpyrazole with methyl iodide and sodium methoxide in methyl alcoholic solution. 1:3-Dimethylpyrazole, b. p. 141—142°, is readily isolated in the homogeneous condition by the dry distillation of its methiodide, m. p. 255—256°. In a similar manner, the ethylation of 3-methylpyrazole with ethyl bromide at 100° or in the presence of alkali gives 3-methyl-1-ethylpyrazole, a colourless liquid, b. p. 132°/atmospheric pressure (*picrate*, slender yellow needles, m. p. 141°); the formation of quaternary salts in this case is much less pronounced than when methyl iodide is used. The products of the benzylation of 3-methylpyrazole are readily separated by taking advantage of the insolubility of the benzylated compounds in water in which the original material and the pyrazolium salt are soluble; experiments in the presence or absence of alkali yielded 1-benzyl-3-methylpyrazole, a colourless liquid with an odour of hyacinths, b. p. 140—141°/14 mm. (*picrate*, slender, yellow needles, m. p. 112.5—113.5°). In contrast to the indazoles, 3-methylpyrazole, when alkylated by different methods, gives only one definite substitution product. The proof that this is a 1:3- (and not a 1:5-) derivative is deduced in the following manner. The benzoic ester of hydroxymethyleneacetone,  $\text{CH}_3\text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{OBz}$ , colourless crystals, m. p. 91—92°, prepared by the action of benzoyl chloride on a suspension of the sodium compound of hydroxymethyleneacetone in pyridine and anhydrous ether) is condensed with methylhydrazine and benzylhydrazine, whereby dimethyl- and benzylmethyl-pyrazoles are obtained identical with the products described above; unfortunately, it was not found possible to isolate the intermediately formed benzoates, but the mode of formation

leaves practically no doubt that 1:3-derivatives are formed. Under similar conditions, phenylhydrazine gives 1-phenyl-3-methylpyrazole, m. p. 37°. The condensation of hydroxymethyleneacetone with methylhydrazine leads to the production of 1:3-dimethylpyrazole without any isomeric substance, and differs therefore from the action with phenylhydrazine, which yields a mixture of 1:3- and 1:5-compounds.

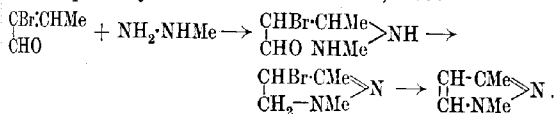
The observations have been extended to 3:5-dimethylpyrazole,  $\text{NH} \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{CH} \\ \text{CH} \end{smallmatrix} \text{Me}$ , the symmetrical structure of which excludes the formation of structurally isomeric 3- and 5-derivatives; any case of isomerism must therefore be due to difference in a ring structure, since the production of 4-derivatives is excluded. It is converted by methyl iodide in the presence of alkali into 1:3:5-trimethylpyrazole, the picrate of which has m. p. 144–145°, whereas Knorr gives 131–133°. Similarly, 3:5-dimethylpyrazole and benzyl chloride at 170° give exclusively 1-benzyl-3:5-dimethylpyrazole, a colourless liquid, b. p. 144–146/10 mm. (picrate, lustrous, greenish-yellow needles, m. p. 126.5–127.5°). The latter compound is also produced by the action of acetylacetone on benzylhydrazine, although in this case the primary production of a three-membered ring might be expected. Finally, 1-phenyl-3:5-dimethylpyrazole has been prepared by the action of phenylhydrazine on acetylacetone and methyl  $\alpha$ -bromopropenyl ketone,  $\text{CHMe}:\text{CBr}:\text{COMe}$ , respectively; the compound obtained in either case gives a picrate, m. p. 101°, and there is no evidence of the production of an isomeric compound.

From the foregoing it appears therefore that cases of isomerism due to the different structure of the ring are not found in the cases of alkylated and arylated pyrazoles. It is, however, still more remarkable that the number of position isomeric alkylpyrazoles is smaller than would be expected from theoretical considerations since 1:3-derivatives are frequently formed exclusively when mixtures of them with 1:5-compounds or when the latter alone would be normally expected. In the hope that the reactions in the pyrazole series would resemble those in the indazole group, an examination of the effect of heat on pyrazolium salts has been made. 1-Phenyl-3-methylpyrazole methiodide, m. p. 144°, and 1-phenyl-5-methylpyrazole methiodide, m. p. 282°, lose methyl iodide when subjected to dry distillation and re-form 1-phenyl-3-methylpyrazole and 1-phenyl-5-methylpyrazole, respectively. Contrary to expectation, however, pure 1:3-dimethylpyrazole and 3-methyl-1-ethylpyrazole are obtained from 1-benzyl-3-methylpyrazole methiodide, m. p. 153–154°, and 1-benzyl-3-methylpyrazole ethiodide, colourless prisms, m. p. 149.5–150.5°. The formation of 1:3- instead of 1:5-compounds discloses a surprising atomic

migration in accordance with the scheme  $\begin{smallmatrix} \text{CH} & \text{CH} \\ | & | \\ \text{CH} \cdot \text{N}(\text{C}_6\text{H}_5) & \text{N} \end{smallmatrix} \begin{smallmatrix} \text{Me} \\ \text{Me}(\text{Et}) \end{smallmatrix} \xrightarrow{+ \text{C}_2\text{H}_5\text{I}} \begin{smallmatrix} \text{CH} & \text{CH} \\ | & | \\ \text{CH} & \text{CH} \end{smallmatrix} \begin{smallmatrix} \text{Me} \\ \text{Me}(\text{Et}) \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{Me} \\ \text{Me}(\text{Et}) \end{smallmatrix}$ . The im-

portance of the observation has caused special attention to be directed to the constitution of the pyrazolium salts. The possibility that, contrary to rule, the addition of alkyl iodide occurs at the nitrogen atom which is already attached to an alkyl group is excluded by the observation that 1-benzyl-3-methylpyrazole methiodide differs from 1:3-dimethylpyrazole benzyl iodide, colourless leaflets, m. p. 167° (corresponding *picrate*, flat, yellow needles, m. p. 126°). The further possibility that the difference in the two iodides is due to the different spatial arrangement of the substituents around the same nitrogen atom and not to structural differences is improbable, and is more definitely excluded by the apparent impossibility of effecting their mutual interconversion. The wandering of alkyl groups during the fission of certain pyrazolium salts must therefore be regarded as established. Nevertheless, it does not follow that 1:5-dialkylpyrazoles are incapable of existence, since the high temperature involved in the fission can greatly facilitate the transformation of the primary products of the change into the 1:3-isomerides.

The synthesis of 1:5-dialkylpyrazoles has therefore been attempted under conditions which are less likely to involve transformation. The action of phenylhydrazine on  $\alpha$ -bromocrotonaldehyde leads to the formation of 1-phenyl-5-methylpyrazone (cf. Vignier, A., 1913, i, 444), but under precisely similar conditions, methylhydrazine gives 1:5-dimethylpyrazole in good yield. A possible explanation of the difference in the reaction lies in the assumption that the alkylhydrazine, unlike the aryl compound, becomes primarily added at the double bond, thus:



This hypothesis is shown to be improbable in the following manner.  $\beta$ -Keto-*n*-butyl alcohol condenses with methylhydrazine sulphate in aqueous solution in the presence of acetic acid and sodium

acetate to yield 1:3-dimethylpyrazoline,  $\begin{array}{l} \text{CH}_2\cdot\text{CH}_2 \\ \text{CMe=N} \end{array} \text{>NMe}$ , a colour-

less liquid, b. p. 127–129° (*picrate*, yellow needles, m. p. 131.5–132.5°) (1-phenyl-3-methylpyrazoline, m. p. 71–72°, is prepared similarly from phenylhydrazine). If crotonaldehyde, which may be assumed to react in the same manner as its bromo-derivative, is similarly condensed with methylhydrazine, it must yield 1:3-dimethylpyrazoline if the hydrazine is added initially at the double bond and 1:5-dimethylpyrazoline if the initial reaction occurs at the aldehyde group. It is found that the compound which is produced is not identical with that derived from  $\beta$ -keto-*n*-butyl alcohol, and hence must be regarded as 1:5-dimethylpyrazoline,  $\begin{array}{l} \text{CH}_2\cdot\text{CHMe} \\ \text{CH=N} \end{array} \text{>NMe}$ ; it is a colourless, very hygroscopic liquid, b. p. 124–125°, which gives a *picrate*, thin, golden-yellow leaflets,

m. p. 113–114°. It must therefore be considered that the production of 1:3-dimethylpyrazole from methylhydrazine and bromocrotonaldehyde instead of the expected 1:5-derivative is actually due to atomic wandering.

Attempts to convert 1:3- and 1:5-dimethylpyrazolines into the corresponding pyrazoles by cautious oxidation with bromine led to remarkable results. The 1:3-compound is transformed smoothly into 1:3-dimethylpyrazole; the 1:5-derivative is largely resinified but is partly converted into 1:3-dimethylpyrazole.

It therefore appears that, under usual conditions, 1:5-dimethylpyrazole (and presumably other 1:5-dialkylpyrazoles) are incapable of existence, whereas 1-phenyl-3-methylpyrazole and 1-phenyl-5-methylpyrazole are stable substances.

Knorr's conception that the pyrazole molecule is symmetrically constituted owing to the oscillation of the double bonds and of the hydrogen atom united to the nitrogen:

$$\begin{array}{c} \text{CH} \cdot \text{NH} \\ \text{CH} \cdot \text{CH} \end{array} \gg \text{N} \rightleftharpoons$$

$\begin{array}{c} \text{CH} = \text{N} \\ \text{CH} \cdot \text{CH} \end{array} \gg \text{NH}$ , can scarcely be extended to the alkyl derivatives

of pyrazole, since a continuous oscillation of an alkyl group between two nitrogen atoms is contrary to all experience of tautomerism and the firmness of attachment of alkyl groups. The authors do not regard the production of 1:3-dialkylpyrazoles in place of the expected 1:5-derivatives as due to the identity of the two series of compounds in consequence of "mobile" double bonds and oscillatory atomic displacements; it is caused by the great instability of the 1:5-derivatives which immediately after formation become

isomerised in accordance with the scheme:

$$\begin{array}{c} \text{CH} = \text{N} \\ \text{CH} \cdot \text{CR} \end{array} \gg \text{NR} \rightarrow$$

$\begin{array}{c} \text{CH} \cdot \text{NR} \\ \text{CH} \cdot \text{CR} \end{array} \gg \text{N}$ .

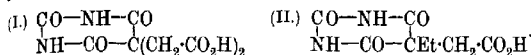
H. W.

**The Polymorphism of Antipyrine, Vanillin, and the Erythritols.** PAUL GAUBERT (*Compt. rend.*, 1922, 175, 1414–1417).—In general, a substance which can be superfused, or, better, can pass into the amorphous state, will occur in several crystalline forms depending on the temperature. This appearance may be favoured by the presence of some impurity or sometimes by the more or less prolonged heating of the substance at a temperature above its melting point. In this manner, it is shown that antipyrine melted on a glass plate may occur in three crystalline modifications, vanillin may give four crystalline modifications, and the erythritols two crystalline forms. The conditions for obtaining these modifications and the forms obtained are detailed.

W. G.

**Preparation of a Derivative of Barbituric Acid Soluble in Water.** HERMANN STAUDINGER (Swiss Pat. 91561; from *Chem. Zentr.*, 1922, iv, 840).—Diallylbarbituric acid or ethylallylbarbituric acid is treated with ozone and the ozonide is changed into the corresponding carboxylic acid. Diallylbarbituric acid gives a crystalline ozonide which is decomposed by heating over a water-bath with

formation of a *dicarboxylic acid* (I), colourless crystals, m. p. 280° (decomp.). Ethylallylbarbituric acid gives similarly a *monocarboxylic acid* (II) which forms colourless crystals, m. p. 280—281°:



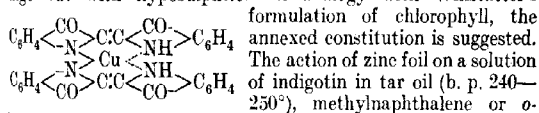
The compounds have therapeutic uses and serve as intermediates for the preparation of other barbituric acid derivatives.

G. W. R.

**Preparation of a Compound of 5-isoPropyl-5-allylbarbituric Acid.** F. HOFFMANN LA ROCHE & Co. (Brit. Pat. 188251).—5-isoPropyl-5-allylbarbituric acid when fused in approximately molecular proportions with 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone form as double compound which is apparently homogeneous, and melts sharply at 92—93°. It is yellow in colour and dissolves in hydrocarbons to a deep yellow solution. Water and other solvents containing hydroxyl give only slightly yellow solutions, indicating that in these solvents the compound is resolved into its colourless components to a considerable extent. The compound is valuable therapeutically, as it combines the soporific action of the barbituric acid with the analgesic action of the pyrazolone, and can therefore partly replace the opiates.

G. F. M.

**Complex Metallic Compounds of Indigotin.** I. K. KUNZ *Ber.*, 1922, 55, [B], 3688—3691).—During the course of experiments on the production of 1:1-diphenylindigotin (Friedländer and Kunz, A., 1922, i, 765), it was observed that boiling solutions of indigotin in *o*-nitrochlorobenzene are rapidly decolorised by cuprous chloride and sodium acetate or copper powder. A similar change is now shown to occur in other solvents of high boiling point. It leads to the formation of the compound,  $\text{C}_{32}\text{H}_{18}\text{O}_4\text{N}_4\text{Cu}$ , which is rapidly decomposed by mineral acids and gives a normal indigo vat with hyposulphite. In analogy with Willstätter's



formulation of chlorophyll, the annexed constitution is suggested. The action of zinc foil on a solution of indigotin in tar oil (b. p. 240—250°), methylnaphthalene or *o*-nitrochlorobenzene leads to the formation of a zinc compound,  $\frac{1}{2}\text{C}_{32}\text{H}_{18}\text{O}_4\text{N}_4\text{Zn}$ , black, lustrous prisms, which, unlike the copper compound, is rapidly hydrolysed by warm water with production of indigotin. A crystalline *nickel* derivative has also been prepared by the use of nickel sulphate and sodium acetate, but it has not yet been found possible to prepare a magnesium compound.

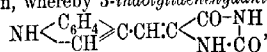
H. W.

**Benzbisthiazoles.** II. STEPHEN RATHBONE HOLDEN EDGE *T.*, 1923, 123, 153—156).

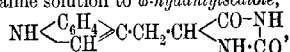
**Syntheses in the Indole Group. I. A New Synthesis of  $\tau$ -Tryptophan.** RIKO MAJIMA and MUNIO KOTAKE (*Ber.*, 1922,

55, [B], 3859—3865).—Indole-3-aldehyde,  $C_6H_4 \begin{smallmatrix} C(CHO) \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} > CH_3$ ,

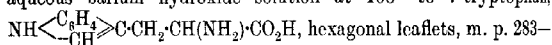
m. p. 193—195°, is conveniently prepared in 40% yield by the successive action of indole and formic ester on a solution of magnesium ethyl iodide in anisole which is cooled in a mixture of ice and salt; in ethereal solution only traces of the aldehyde are formed (cf. Alessandri and Florence, A., 1915, i, 452). Phenetole may replace anisole, and ethoxymethylethaniline may take the place of formic ester, but the yields are thereby somewhat reduced; amyl ether is as unsuitable as ethyl ether. The aldehyde is heated with hydantoin, anhydrous sodium acetate, and acetic anhydride at 106—108°, and the product is treated with aqueous sodium hydroxide solution, whereby 3-indolyldenehydantoin,



m. p. about 320°, decomp. 325°, is formed, the yield being 46.6% of that theoretically possible. 1-Acetylindole-3-aldehyde is obtained as a by-product of the action; it therefore appears probable that it is this derivative which actually undergoes condensation and that acetyl-3-indolyldenehydantoin is hydrolysed by the treatment with sodium hydroxide; the inefficiency of acetic acid and sodium acetate as condensing agents thus receives an explanation. 3-Indolyldenehydantoin is reduced by sodium amalgam in alkaline solution to  $\omega$ -hydantylscatole,



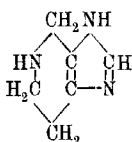
colourless needles, m. p. 220—221°. The latter is hydrolysed by aqueous barium hydroxide solution at 108° to  $\tau$ -tryptophan,



285° after becoming discoloured at 250°. As by-product, a substance,  $C_{12}H_{13}O_3N_3$ , leaflets, m. p. 207° (decomp.), is isolated.

H. W.

**Preparation of a Condensation Product from  $\beta$ -Iminazolyethylamine [4- $\beta$ -Aminoethylglyoxaline].** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92297; from *Chem. Zentr.*, 1922, iv, 890).—When formaldehyde or, preferably, methylal is added slowly to a suspension of



line and has m. p. 249°.

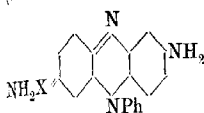
4- $\beta$ -aminoethylglyoxaline in fuming hydrochloric acid at 100° and the mixture heated for several hours in a reflux apparatus,  $\beta$ -imidazolydisopiperidine [tetrahydro-1:3:6-benzotriazole] (annexed formula) is formed. The hydrochloride is crystalline and has m. p. 249°.

G. W. R.

**Determination of the Constitution of Colouring Matters from their Absorption Spectra. IV.** F. KEHRMANN and M. SANDOZ (*Helv. Chim. Acta*, 1922, 5, 895—905; cf. A., 1921, i, 276).—In continuation of previous work, the absorption spectra of

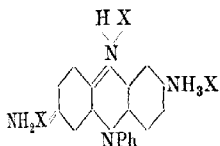
salts of diamino-derivatives of methyl- and phenyl-phenazine have been examined. The introduction of a second symmetrical amino-group into the monoaminomethylphenazine previously described (*loc. cit.*), lightens the colour of the mono-acid salt from cherry-red to orange-red. The absorption maxima are at  $\lambda$  530 and  $\lambda$  483. Introduction of a phenyl group into each amino-group deepens the shade to bluish-violet, and there is now only one absorption maximum, at  $\lambda$  572. The corresponding ditolyl derivative has an absorption maximum at  $\lambda$  580.

The monoacid salts of the diaminophenylphenazines chosen for examination were the perchlorates, on account of their great stability. The mono-acid salt of 2:7-diaminophenylphenazine (annexed formula) is blue, and to it may be ascribed the same



para-quinonoid structure as to *aposafranine*, which is violet-red. The di-acid salt is red, corresponding very closely with *aposafranine*, from which it is inferred that the second amino-group has been neutralised but that no change in the

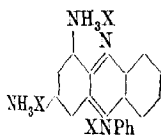
disposition of the double bonds has occurred. When the diaminophenylphenazonium perchlorate is dissolved in concentrated sulphuric acid, the colour of the solution is green. The colour is due



to the tri-acid salt (annexed formula) and is similar to that of the di-acid salt of *aposafranine*. Again there is no change of structure, and it is interesting to note the colour-deepening effect of the fixation of an equivalent of acid by a doubly-linked atom forming part of the chromogen. Finally,

in fuming sulphuric acid the colour is reddish-brown, resembling the di-acid salt of phenylphenazine. This salt must have an ortho-quinonoid structure.

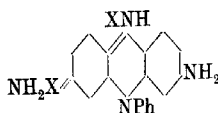
The perchlorate of 1:3-diaminophenylphenazine is green in water, yellowish-green in alcohol, approaching a yellow of the second order. Although the amino-group in position 1 has a considerable colour-deepening effect, the structure is still probably paraquinonoid. The di-acid salt of this compound resembles



*aposafranine*, as in the case of the 2:7-isomeride, but the tri-acid salt, obtained by direct solution in concentrated sulphuric acid, is not green, but yellow, resembling the mono-acid salt of phenylphenazine. The structure of this salt must therefore be orthoquinonoid (annexed formula). When the perchlorate is dissolved in fuming sulphuric acid, the reddish-brown colour of the tetra-acid salt is obtained.

The perchlorate of the third isomeride, *phenosafranine*, is red with an orange fluorescence in solution. Here again, as with methylphenazine, the second symmetrical amino-group brightens the shade whilst the colour intensity is increased. The di-acid

salt is blue, indicating that the second acid equivalent is combined with chromogenic nitrogen (annexed formula). The tri-acid salt



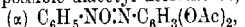
is green, resembling, as expected, the di-acid salt of *aposafranine*. The tetra-acid salt is the normal reddish-brown. It is concluded that all the observed facts can be explained if it is granted that two states, ortho- and para-quinonoid, are possible in this series. It is further shown briefly that acetylation of an amino-group in this series has a similar effect on its auxochromic properties to neutralisation of the group with acid.

E. H. R.

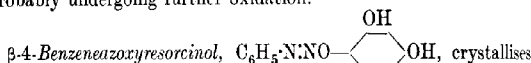
**The Solubility of the Salts of Uric Acid.** GEORG BARKAN (*Z. Biol.*, 1922, **76**, 257—266).—The solubility of freshly precipitated amorphous sodium urate ( $C_5H_3O_3N_4Na \cdot H_2O$ ) at  $18^\circ$  is 2.03 g. or  $9.8 \times 10^{-3}$  gram-molecules per litre. On keeping, or more particularly on stirring in contact with its solution, the solubility decreases, and approaches that of the crystalline form.

W. O. K.

**Oxidation of Benzeneazoresorcinol.** DINO BIGIARI and GIULIO GIANNINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 109—116).—Of the two possible diacetyl derivatives,

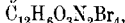
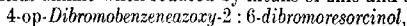


and ( $\beta$ )  $C_6H_5 \cdot N \cdot NO \cdot C_6H_3(OAc)_2$ , obtainable by the oxidation of the diacetyl compound of benzeneazoresorcinol by means of hydrogen peroxide, only the latter is actually obtained, the  $\alpha$ -form probably undergoing further oxidation.

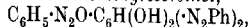
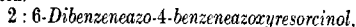


in red granules, m. p.  $144^\circ$ , giving a chestnut-yellow powder. The *dibenzoyl* derivative forms pale yellow needles, m. p.  $113^\circ$ , and the *diacetyl* derivative, long, pale yellow, silky needles, m. p.  $102^\circ$ .

4-Benzeneazoxy-2:6-dibromoresorcinol,  $C_6H_5 \cdot N \cdot NO \cdot C_6H_3Br_2(OH)_2$ , crystallises in transparent, greenish-yellow cubes, m. p.  $153^\circ$ , and yields aniline when reduced by means of zinc and acetic acid.



forms long, red needles, m. p.  $229^\circ$  (decomp.), and gives 2:4-dibromoaniline when reduced by means of tin and hydrochloric acid.



is a red compound, m. p.  $220^\circ$ .

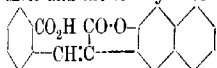
When treated with alcoholic potassium hydroxide, the diacetyl derivative of  $\beta$ -benzeneazoxyresorcinol yields a dark red compound, m. p. about  $190^\circ$ , which has not yet been characterised.

T. H. P.

**Oxidation of Benzeneazonnaphthols.** I. DINO BIGIARI and RENATO CERCHIAI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 27—30).—Owing to the divergent behaviour towards alkali shown by the three isomeric benzeneazonnaphthols, a phenylhydrazonic constitution is attributed to 1-benzeneazo-2-naphthol, whilst 4-benzeneazo-1-naphthol and 2-benzeneazo-1-naphthol are considered to possess the ordinary hydroxylic formulæ (Goldschmidt and Brubacher, A., 1891, 1209; Willstätter and Parnas, A., 1907, i, 425, 1056). Marked differences are found also in the behaviour of these compounds towards 30% hydrogen peroxide solution and acetic acid.

Thus, under these conditions, 1-benzeneazo-2-naphthol and also its acetyl-derivative undergo slow oxidation in the cold to carboxycinnamic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , m. p.  $200^\circ$ , whilst in the hot they yield the isomeric dihydroisocoumarincarboxylic acid,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO-O} \\ \diagup \end{smallmatrix} \text{CH}_2\begin{smallmatrix} \diagdown \\ \text{CH}\cdot\text{CO}_2\text{H} \end{smallmatrix}$ , m. p.  $153^\circ$ , which is also obtained when carboxycinnamic acid is fused for a few moments.

Similar oxidation of  $\beta$ -naphthol yields the products obtained by Ehrlich by the action of permanganate (A., 1889, 1001), namely: (1) Carboxycinnamic acid, for which, however, this author gave m. p.  $183^\circ$  instead of  $200^\circ$ ; (2) an acid,  $\text{C}_{20}\text{H}_{12}\text{O}_4$ , m. p.  $281^\circ$ , which, although regarded by Ehrlich as dibasic, gives only mono-silver and monoethyl derivatives, and has probably the structure

. This acid reduces permanganate, but not so rapidly as does carboxycinnamic acid.

T. H. P.

**Reduction of Ethyl Diazobenzylideneglucuronate.** P. A. LEVENE (*J. Biol. Chem.*, 1922, **54**, 809—813).—When reduced with aluminium amalgam in isopropyl-alcoholic solution, ethyl diazobenzylideneglucuronate yields a mixture of ethyl benzylidenedeoxyglucuronate and ethyl benzylidene chitosamate. The former product is identical with that previously obtained (A., 1922, i, 1028) by reduction of ethyl benzylidene- $\alpha$ -3-anhydromannonate; the latter was not isolated, but was identified by hydrolysis into chitosamic acid. The reduction apparently takes place asymmetrically, for no trace of an epimeride of chitosamic acid can be detected. That the deoxy-compound is not produced through the intermediate formation of an unsaturated compound is shown by the fact that the amide of benzylidene- $\alpha$ -3-anhydromannonic acid is unchanged when submitted to similar treatment.

E. S.

**The Formation of Aromatic Thiocyanates by the Diazo-reaction.** A. KORCZYNSKI [with J. KNIATOWNA and F. KAMINSKI] (*Bull. Soc. chim.*, 1922, [iv], **31**, 1179—1185).—In the transformation of *o*-nitrodiazobenzene thiocyanate into *o*-nitrophenyl thiocyanate under the catalytic influence of a metallic thiocyanate, the yield obtained depends on the metal of which a salt is used and on the temperature, being greater, in the majority of cases

studied, at 15–20° than at 60–70°. The most effective catalysts of the substances used are the thiocyanates of iron and tungsten.

H. J. E.

**The Tryptophan Content of some Proteins.** CLARENCE E. MAY and EMBREE R. ROSE (*J. Biol. Chem.*, 1922, **54**, 213–216).—The colour which tryptophan yields with Ehrlich's reagent has been utilised for the estimation. The protein (0.05 to 1 g.) is added to a mixture of concentrated hydrochloric acid (50 c.c.), water (50 c.c.), and a 5% solution of *p*-dimethylaminobenzaldehyde in 10% sulphuric acid (1 c.c.). It is then incubated at 35° for twenty-four hours, left at the ordinary temperature for at least twenty-four hours, and the colour then compared with a casein standard. It is assumed that casein yields 1.5% of tryptophan. Application of the method to a number of proteins yielded the following values: lactalbumin 2.4, gliadin 1.05, glutenin 1.80, edestin 1.5, glycinin 1.65, ovovitellin 1.74, egg-albumin 1.11, phaseolin 0.80, maize gluten 1.08, legumin (vetch) 1.05%. No colour developed in the case of zein and gelatin.

E. S.

**The Isoelectric Point of Globin.** SHUNGO OSATO (*Biochem. Z.*, 1922, **132**, 485–487).—The isoelectric point of globin from blood-corpuscles is found by the precipitation method to be at  $P_H$  8.1.

W. O. K.

**I. The Preparation of Nucleic Acid from the Nucleoprotein of Tubercle Bacilli (Tuberculinic Acid). II. The Pyrimidines contained in Tuberculinic Acid, the Nucleic Acid of Tubercle Bacilli.** TREAT B. JOHNSON and ELMER B. BROWN (*J. Biol. Chem.*, 1922, **54**, 721–730, 731–737).—I. A method is described for the preparation of tuberculinic acid from tubercle bacilli (cf. also Ruppel, A., 1899, ii, 237; Levene, A., 1901, i, 299). The protein which remains after removal of this nucleic acid has been analysed for nitrogen distribution with the following results: amide-N 11.83, humin-N 4.11, cystine-N 1.26, arginine-N 10.63, histidine-N 11.48, lysine-N 3.69, monoamino-N 47.39, non-amino-N 9.34%. Tryptophan was also present.

II. Cytosine and thymine have been isolated from the products of hydrolysis of tuberculinic acid; the presence of uracil could not be detected.

E. S.

**The Results and Aims of General Enzyme Chemistry.** H. VON EULER (*Ber.*, 1922, **55**, [B], 3583–3600).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Aerzte*.

H. W.

**The Isolation of Enzymes.** RICHARD WILLSTÄTTER (*Ber.*, 1922, **55**, [B], 3601–3623).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Aerzte*.

H. W.

**Saccharase.** E. CANALS (*Bull. Soc. chim.*, 1922, [iv], **31**, 1333–1341; cf. A., 1922, i, 1075).—The author traces a relationship between the magnesium and phosphate content of saccharases of various origins, and their respective diastatic powers, which

seems to some extent to support the opinion of Salkowski that invertase is the magnesium salt of a nitrogenous phosphated acid. A direct relationship cannot be traced, however, between the total magnesium and phosphoric acid content and the diastatic power, since, if the preparation is purified by dialysis, the diastatic power is enhanced whilst there is a loss of about 40% of Mg and 8% of  $P_2O_5$ , and all the magnesium and phosphoric acid of the saccharase is therefore not essential for the hydrolysing activity. Purification by precipitation with alcohol results in a similar loss in magnesium and an even greater loss in phosphoric acid, and in this case the diastatic power is greatly diminished, owing probably to a profound modification of the colloidal system of the enzyme by this treatment. Alcoholic precipitation is therefore not suitable for the purification of saccharase. It is observed that the magnesium of the saccharase dialyses less easily, and is less readily separated by alcoholic precipitation than the phosphate, and it would therefore seem to enter to a greater extent into the constitution of the micelle.

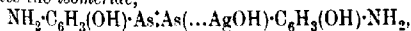
G. F. M.

**The Influence of Neutral Alkali-metal Salts on Diastatic Ferment.** V. AMANDUS HAHN and HUGO MEYER (*Z. Biol.*, 1922, 76, 227—246).—Purified diastase from commercial pancreatin "Rhenania" is influenced as regards its activity by the presence of neutral salts of the alkali metals similarly to saliva diastase, and to unpurified pancreatin. The optimum  $P_H$  depends on the buffer solution used, being 7.2 with a phosphate mixture and 5.6 with an acetate mixture, resembling saliva which has corresponding optimum at  $P_H$  6.6 and  $P_H$  5.6. The influence of neutral salts is much more marked with acetate buffer mixtures than with phosphate buffer mixtures. In both cases the effect is to increase the optimum  $P_H$ .

W. O. K.

**Arseno-metallic Compounds. II. Isomeric Silver Salvarsans.** A. BINZ and W. H. LUDWIG (*Ber.*, 1922, 55, [B], 3826—3831).—The silver complex of silver salvarsan has been considered by Ehrlich and Karrer (*A.*, 1916, i, 95) to be co-ordinatively attached to the arsenic atom and by Binz, Bauer, and Hallstein (*A.*, 1920, i, 401) as united by the residual affinity of the nitrogen atom. The isolation of two isomeric silver salvarsans apparently justifies both formulæ. At present, the allotment of the structure to the isomeride is somewhat arbitrary and is due to the fact that one form is lighter in colour than the other and resembles to this extent the complex compounds containing silver and nitrogen, but not arsenic.

*Silver salvarsan I*,  $NH_2 \cdot C_6H_3(OH) \cdot As \cdot As \cdot C_6H_3(OH) \cdot NH_2 \dots AgOH$ , is obtained by adding sodium carbonate solution to salvarsan and silver nitrate dissolved in water; it is insoluble in sodium carbonate and stable towards reduction with hypophosphorous acid. It dissolves in sodium hydroxide solution with the dark brown colour of technical silver salvarsan, and from the solution carbon dioxide precipitates the *isomeride*,



a dark brown substance which dissolves in sodium carbonate solution and is reduced by hypophosphorous acid. Silver salvarsan I is rapidly converted by hydrochloric acid into the compound  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2\cdots\text{AgCl}$ , a pale yellow powder. The dark brown isomeride II appears to be unaffected by similar treatment after several hours, but gradually becomes converted into the chloride just described, the formation of which from the chloride,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{As}\cdot\text{As}(\cdots\text{AgCl})\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2$ , takes place very slowly in comparison with the change in the reverse direction in alkaline solution. The same change occurs when solutions of technical silver salvarsan are treated with hydrochloric acid, the brown colour in this case persisting for a considerable time and gradually giving place to a pale yellow precipitate. H. W.

### Physiological Chemistry.

#### Respiratory Exchange in Fresh-water Fish. IV. Further Comparison of Gold-fish and Trout. JOHN ADDYMAN GARDNER

and GEORGE KING (*Biochem. J.*, 1922, **16**, 729—735).—The oxygen tension at the asphyxial point at various temperatures in the case of the gold-fish has been determined. This fish can stand much lower oxygen tensions for any temperature than the trout. The difference is more marked at low temperatures. Trout kept at a low temperature corresponding with a state of hibernation showed a higher glycogen content than control fish kept at higher temperatures, which is consonant with the respiratory coefficients obtained for these fish. Glycogen estimation in the case of the gold-fish yielded results which were in conformity with the low level of their metabolism. S. S. Z.

#### Respiratory Exchange in Fresh-water Fish. V. Eels.

JOHN ADDYMAN GARDNER and GEORGE KING (*Biochem. J.*, 1922, **16**, 736—738).—Eels live at a much lower plane of metabolism than trout. At medium temperatures trout use about four times as much oxygen as eels, and at low temperatures 10—12 times as much. S. S. Z.

**Influence of the Introduction of Water on Blood Concentration Induced by Deprivation of Water.** FRANK P. UNDERHILL and ROBERT KAPSINOW (*J. Biol. Chem.*, 1922, **54**, 459—464).—The experiments were performed on dogs. Deprivation of water for short intervals produced an increased blood concentration which rapidly returned to approximately the normal on administration of water. E. S.

**Gas and Electrolyte Equilibria in the Blood. III. The Alkali-binding and Buffer Values of Oxyhæmoglobin and Reduced Hæmoglobin.** DONALD D. VAN SLYKE, A. BAIRD HASTINGS, MICHAEL HEIDELBERGER, and JAMES M. NEILL (*J. Biol. Chem.*, 1922, **54**, 481—506).—The technique previously developed

(A., 1922, i, 1207) has been used to determine the amount of alkali bound both by recrystallised horse oxyhæmoglobin (Heidelberger, A., 1922, i, 962) and by reduced hæmoglobin when under physiological conditions of concentration, carbon dioxide tension, and  $P_{H_2}$  value. At  $P_{H_2}$  7.4 one gram-molecule of oxyhæmoglobin binds  $2.15 \pm 0.10$  equivalents of alkali (sodium) whilst the corresponding figure for reduced hæmoglobin is  $1.47 \pm 0.08$ . The change of one mol. of reduced hæmoglobin to oxyhæmoglobin thus enables it to combine with an additional  $0.68 \pm 0.10$  equivalent of alkali. At intermediate points the increase in base bound is directly proportional to the increase in oxygen content, thus agreeing with Henderson's theory (A., 1921, i, 473) and with the assumption originally made by Christiansen, Douglas, and Haldane (A., 1914, i, 1012). The molecular buffer values (cf. A., 1922, i, 893) of oxyhæmoglobin and reduced hæmoglobin are practically constant over the physiological range of  $P_{H_2}$ , that for the former being  $\beta_{H_2} = 2.64$  and for the latter  $\beta_{H_2} = 2.45$ . The authors conclude from these values that the alkali taken up by hæmoglobin is shared between at least five univalent acid groups. The total amount of base bound by hæmoglobin at  $P_{H_2}$  values varying from 7.2 to 7.5 is given by the equation:  $B = 2.64[HbO_2](P_{H_2} - 6.585) + 2.45[Hb](P_{H_2} - 6.80)$ . E. S.

**Gas and Electrolyte Equilibria in the Blood. IV. The Effect of Oxygenation and Reduction on the Bicarbonate Content and Buffer Value of Blood.** DONALD D. VAN SLYKE, A. BAIRD HASTINGS, and JAMES M. NEILL (*J. Biol. Chem.*, 1922, 54, 507-526).—The experiments recorded in the previous paper have been extended to oxygenated and reduced horse blood (oxalated or defibrinated). Since carbonic acid and hæmoglobin are the only acids present in blood, the assumption has been made, in interpreting the results, that changes in the amount of base present as bicarbonate are accompanied by equal and opposite changes in the amount combined with hæmoglobin. The results show that each specimen of blood, when at the same degree of oxygenation, has a constant buffer value over the  $P_{H_2}$  range 7.2 to 7.5, the average values of different specimens being 25.3 for oxygenated blood and 24.4 for reduced blood (buffer values are here expressed as millimols. of base per unit change in  $P_{H_2}$ ; cf. A., 1922, i, 893). The difference between these two values is due to the loss of buffer value which occurs when oxyhæmoglobin is reduced (cf. preceding abstract), a loss which is partly compensated for by an increase in bicarbonate content. Thus, of the total buffer value, hæmoglobin was responsible for 76.0% and bicarbonate for 6.9% in oxygenated blood, the figures for reduced blood being 73.3% and 9.0%, respectively. Each additional molecule of oxygen taken up by hæmoglobin at  $P_{H_2}$  7.3 caused decreases in the bicarbonate content varying from 0.50 to 0.59 in different specimens. On the above assumption, a mol. of hæmoglobin when changed from the reduced to the oxygenated state therefore combines with an additional 0.50-0.59 equivalent of alkali. This value differs

from that obtained with solutions of crystallised hæmoglobin and is hence probably influenced by some unknown variable factor in blood. As for solutions of hæmoglobin, the amount of additional base combined with hæmoglobin in blood on oxygenation was directly proportional to the amount of oxygen combined. Over the range  $P_H$  7.2 to 7.5 a rise of  $P_H$  0.1 caused an increase of approximately 0.02 equivalent in the amount of base transferred from bicarbonate to hæmoglobin by one molecule of oxygen. E. S.

**Evaluation of Buffers of the Blood.** EDWARD A. DOISY, A. P. BRIGGS, EMILY P. EATON, and WILLIAM H. CHAMBERS (*J. Biol. Chem.*, 1922, 54, 305—329).—The authors have investigated the extent to which the various known buffer systems of the blood participate in binding carbon dioxide during the change of blood from the arterial to the venous state. In the results obtained from three specimens of human blood, from 87—95% of the carbon dioxide has been accounted for. Of the total amount taken up, 75—80% was due to the hæmoglobin, less than 1% to the inorganic phosphates, and less than 5% to the buffers contained in the separated serum. E. S.

**Measurement of the Alkalinity of the Blood.** CH. O. GULLAUMIN (*J. Pharm. Chim.*, 1923, [vii], 27, 5—23).—For the measurement of the  $P_H$  of the blood and the alkaline reserve, the methods described by Cullen (*J. Biol. Chem.*, 1922, 52, 508) with very slight modifications give accurate results with inexpensive apparatus. H. K.

**Relations Existing between Arterial and Venous Blood of the Dog with Special Reference to the Plasma Chlorides.** EDWARD A. DOISY and J. W. BECKMANN (*J. Biol. Chem.*, 1922, 54, 683—691).—Analyses were made of arterial and venous blood drawn simultaneously from dogs. The results show that the migration of hydrochloric acid from plasma to corpuscles, which is to a large extent responsible for the buffer action of blood in vitro (cf. A., 1922, i, 963), occurs also in vivo as blood passes from the arterial to the venous state. Evidence was also obtained, although the results were less consistent, that the blood respiratory coefficient has a normal value, that the additional carbon dioxide contained in venous blood is approximately equally distributed between plasma and corpuscles, and that the corpuscles occupy a larger volume in venous than in arterial blood. E. S.

**Non-protein Organic Constituents in the Blood of Marine Fish.** W. DENIS (*J. Biol. Chem.*, 1922, 54, 693—700).—Analyses previously made (A., 1914, i, 106) have been repeated using recent methods. The following are the average results, expressed in mg. per 100 c.c. of blood, for different species of elasmobranch and teleost fishes: Elasmobranch blood—non-protein nitrogen, 1000; urea nitrogen 800; amino-nitrogen 28; creatinine 6; creatine 25; uric acid 1.1. Teleost blood—non-protein nitrogen 65; urea nitrogen 9; amino-nitrogen 28; creatinine 1.0; creatine 6; uric acid 4. The blood of invertebrates was found frequently to contain

20 amino-nitrogen although considerable amounts were present  
in the muscle. E. S.

**The Neutrality of Blood.** J. MELLANBY and C. C. WOOD (*Proc. Physiol. Soc.*, 1922, lii-lii; *J. Physiol.*, 1922, 56; from *Physiol. Abstr.*, 1922, 7, 490).—Corpuscles, partly freed from carbon dioxide and suspended in 0.85% sodium chloride solution, have a slightly acid reaction. When exposed to alveolar air, these corpuscles absorb carbon dioxide and the reaction tends to neutrality. On the other hand, serum from the same blood is alkaline in reaction and on exposure to alveolar air becomes more acidic. This apparently paradoxical effect of carbon dioxide explains the approximate neutrality of the blood under varying tensions of carbon dioxide, and perhaps also the divergence which exists between the calculated reaction of the blood, based on the ratio of the free and combined carbon dioxide contained in it and that actually observed by direct experiment. W. O. K.

**Combined Uric Acid in Ox Blood.** ALICE ROHDE DAVIS, ELEANOR B. NEWTON, and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, 54, 595—599).—The uric acid compound present in the corpuscles of ox blood (cf. A., 1915, i, 612) has been isolated. It forms square plates which do not melt under 300°, and when hydrolysed with sulphuric acid yields equimolecular quantities of uric acid and *d*-ribose. It is apparently a monobasic acid; its sodium salt has  $[\alpha]_D^{20} + 20.42^\circ$ . E. S.

**Distribution of the Combined Uric Acid in the Corpuscles of Ox Blood.** ELEANOR B. NEWTON and ALICE ROHDE DAVIS (*J. Biol. Chem.*, 1922, 54, 601—602).—The combined uric acid (cf. preceding abstract) is present entirely in the erythrocytes. E. S.

**Combined Uric Acid in Human, Horse, Sheep, Pig, Dog, and Chicken Blood.** ELEANOR B. NEWTON and ALICE ROHDE DAVIS (*J. Biol. Chem.*, 1922, 54, 603—605).—The combined uric acid compound (cf. preceding abstracts) seems to be present in the blood of all the above species but in much smaller amounts than in ox blood. E. S.

**Influence of Subcutaneous Injections of Indole and Scatole on the Nitrogenous Metabolism of the Rabbit.** FRANK P. UNDERHILL and ROBERT KAPINOW (*J. Biol. Chem.*, 1922, 54, 717—720).—Using doses of 30 mg. per kg., no influence was observed. Indole, but not scatole, apparently increased the excretion of ethereal sulphates. E. S.

**Inorganic Metabolism. I. Inter-relations between Calcium and Magnesium Metabolism.** L. JEAN BOGERT and ELIZABETH J. MCKITTRICK (*J. Biol. Chem.*, 1922, 54, 363—374).—The addition of magnesium citrate in amounts of 6 g. per day to the diet of four subjects caused an increased excretion of magnesium both in the urine and faeces. There was also an increase in each case in the total calcium excreted, and, in three out of the four

cases, in both urinary and faecal calcium. The similar addition of calcium lactate caused increase in both urinary and faecal calcium. There was probably also an increased excretion of magnesium.

E. S.

**Inorganic Metabolism. II. Effects of Acid-forming and Base-forming Diets on Calcium Metabolism.** L. JEAN BOGERT and ELIZABETH E. KIRKPATRICK (*J. Biol. Chem.*, 1922, **54**, 375—386).—Although certain irregularities occurred, the results, in the main, indicate that acid-forming diets divert calcium from the faeces to the urine and also cause an increased total excretion. Base-forming diets, on the other hand, divert calcium from the urine to the faeces and produce a diminution in the total excretion.

E. S.

**Inorganic Metabolism. III. Influence of Yeast and Butter Fat upon Calcium Assimilation.** L. JEAN BOGERT and RUTH K. TRAIL (*J. Biol. Chem.*, 1922, **54**, 387—397).—In the case of four women, the addition of either yeast or butter fat to a diet which was otherwise vitamin-free produced an increased retention of calcium. The amount of calcium excreted in the faeces was diminished.

E. S.

**Antiketogenesis. IV. The Ketogenic-Antiketogenic Balance in Man and its Significance in Diabetes.** PHILIP A. SHAFFER (*J. Biol. Chem.*, 1922, **54**, 399—441).—Further work on the ketolytic reaction in vitro (cf. A., 1921, i, 754) has shown that, under proper conditions, one molecule of dextrose accomplishes the disappearance of two molecules of acetoacetic acid when the latter is in excess. On this basis, the values previously assigned (A., 1922, i, 83) to the antiketogenic factors must be doubled. This conclusion is supported by the results obtained by Wilder and Winter (A., 1922, i, 893), but when applied to cases taken from the literature it leads to a calculated excretion of acetone substances which is considerably smaller than that actually found. The protein ketogenic factor has therefore been arbitrarily increased by 50%. With this modification, moderate agreement between the calculated and actual values has been obtained. In cases of severe ketosis (where the acetoacetic acid is in excess), each molecule of dextrose appears, without doubt, to be equivalent ketolytic substance for two molecules of keto-acid. At the threshold of ketosis, however, the dextrose molecule may have a lower value owing to oxidation taking place without its coming into contact with the keto-acid. The author discusses the bearing of these results on the dietetic problem of diabetes.

E. S.

**Colorimetric Researches on Tryptophan. VII. The Tryptophan Requirements of Growing Rats (a Contribution to the Question of Cyclopoiesis).** OTTO FÜRTH and FRIEZ LIEBEN (*Biochem. Z.*, 1922, **132**, 325—341).—Only a small fraction (3—8%) of the tryptophan consumed by rats is retained in the

body, the rest being destroyed. The minimal tryptophan requirement for rats per kg. of body weight is greater than for man.

W. O. K.

**Physical Chemistry of Foodstuffs. Investigation of Acid-taste.** THEODOR PAUL (*Z. Elektrochem.*, 1922, 28, 435—446).—By the employment of the methods of psychophysics, and the introduction of a new terminology, the measurement of acid-taste has been placed on a quantitative basis. Molecular acidity is defined as the number of mols. of hydrochloric acid, dissolved in a fixed volume of water, which tastes as acid as one mol. of the acid substance dissolved in the same volume of water. The molecular acidity is determined, not only by the hydrogen-ion concentration, but also by the capacity of the solute to yield its reserve of hydrogen-ions to the tongue, and, to some extent, by the nature of the anion and the vapour pressure of the acid. The acids investigated have been arranged in a series of increasing molecular acidities, thus: carbonic acid, potassium hydrogen tartrate, acetic acid, lactic acid,  $\alpha$ -acetoxypropionic acid, hydrochloric acid, and tartaric acid. In this series, carbonic acid possesses the weakest, and tartaric acid the strongest acid taste. This order is not in agreement with the dissociation constants of these acids. For example, the two acids,  $\alpha$ -acetoxypropionic and tartaric acids, although possessing very similar dissociation constants, show very different molecular acidities. The molecular acidity decreases slowly with increase in concentration. The curves obtained by plotting acid taste against concentration show several points of resemblance with the "sweetness" curves of "saccharin" and dulcin. The two properties, acid-taste and sweetness, behave in an analogous manner with increase in concentration, and this suggests that similar relationships may exist between these and the salt and bitter qualities of substances.

W. E. G.

**The Course of Oxidative Processes [in the Cell].** HEINRICH VIELAND (*Ber.*, 1922, 55, [B], 3639—3648).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Ärzte*.

H. W.

**Glutathione. II. A Thermostable Oxidation-Reduction System.** F. GOWLAND HOPKINS and M. DIXON (*J. Biol. Chem.*, 1922, 54, 527—563).—A continuation of the investigation of the recently discovered glutathione (A., 1921, i, 635) has shown that, in its functions in the cell, this dipeptide is mainly associated with insoluble, thermostable agents which act as hydrogen donors and form with it the thermostable reducing system of the tissues. Thus, tissue which has been extracted with water, treated repeatedly with boiling water or alternatively heated for three hours at 100°, dehydrated with alcohol, and finally dried in a vacuum, all the operations being performed anaerobically, when ground and suspended in a phosphate buffer mixture ( $P_H$  7—8) containing oxidised glutathione is able rapidly to reduce methylene-blue, that portion of its reducing power which depends on the presence of the di-

peptide being practically unaffected by this treatment. The thermostable agents are, however, sensitive to oxidation (for example, by hydrogen peroxide) and are even slowly destroyed by molecular oxygen. The latter effect is enormously accelerated by the presence of glutathione. When suspensions of muscular tissue, prepared as above, are aerated in the presence of the dipeptide oxygen is absorbed to the extent of 400 c.mm. for every gram of dry material used. At the same time carbon dioxide is given off, the "respiratory quotient" of the process being about unity at first and falling off considerably during the later stages. These results suggest that a thermostable mechanism for oxidations and reductions coexists with the specialised enzymic mechanism in living tissue.

E. S.

**Proportion of Sulphur in the Skin of Children Aged Less than One Year.** E. LABORDE (*Bull. Soc. Chim. biol.*, 1922, 4, 584—586).—In the skin of three children approximately 0.2% of sulphur was found. In the healthy skin of another who had died from poisoning by sulphuric acid, there was 0.15%, whilst the burned areas of the skin contained 0.37%.

W. O. K.

**Chemistry of the Liver.** UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 132, 343—351).—An analysis of the fats in horse liver shows the presence of kephalin, lecithin, myristic acid, butyric acid, and other fatty acids, and certain glycerol and cholesterol esters.

W. O. K.

**The Proteolytic Enzymes of the Spleen.** S. G. HEDIN (*J. Biol. Chem.*, 1922, 54, 177—202).—At least three enzymes, namely,  $\alpha$ -protease,  $\beta$ -protease, and crepsin, are present in the spleen of the ox (cf. A., 1904, ii, 58; Morse, A., 1917, i, 606; Dornby, A., 1918, i, 464). A partial separation of these has been effected by extracting the minced spleen successively with dilute acetic acid, casein, and 5% sodium chloride. The acetic acid extract contains all three enzymes; the casein extract contains mainly  $\beta$ -protease and erepsin; whilst a solution in sodium hydroxide of the globulin obtained from the sodium chloride extract contains mainly  $\alpha$ -protease. If the spleen is kept for any length of time in alkaline solution or at an acidity less than  $P_H$  5.2, the enzymes show a loss of activity which cannot be revived by acids.  $\alpha$ -Protease, which acts in alkaline solution, converts proteins into peptones more rapidly than peptones into amino-acids; its action is inhibited by serum-albumin (cf. also Bradley, A., 1922, i, 896).

E. S.

**The Catalytic Destruction of Carnosine in Vitro.** WINIFRED MARY CLIFFORD (*Biochem. J.*, 1922, 16, 792—799).—A catalyst is described which is capable of destroying carnosine in muscle extract. It is present in ox, rat, and cod muscle, but is absent in the muscle of invertebrates such as the oyster and the lobster. It is also present in the liver of the rat and of the ox. The kidney of the rat, ox, or sheep does not contain it. The curve of action of this catalyst is unlike any enzyme curve. The possible mechanism of

its action is discussed. It is also suggested that carnosine may be an intermediate product of metabolism. S. S. Z.

**Excretion of Acid and Ammonia.** ROGER S. HUBBARD and SAMUEL A. MUNFORD (*J. Biol. Chem.*, 1922, **54**, 465—479).—From a statistical analysis of the results of a series of analyses of human urine the authors conclude that the excretion of ammonia varies with the volume and the reaction of the urine but is not directly affected by the amount of acid excreted. The relation between the reaction of the urine and the excretion of ammonia is concerned rather with the concentration of the ammonia than with the actual amount excreted. The latter fact is interpreted as supporting the theory (Nash and Benedict, A., 1922, i, 191, 483) that the kidney is the seat of formation of ammonia. E. S.

**The Influence of Fat and Carbohydrate on the Nitrogen Distribution in the Urine.** EDWARD PROVAN CATHCART (*Biochem. J.*, 1922, **16**, 747—753).—The output of total nitrogen, urea, and ammonia rises on a fat diet and falls on the addition of carbohydrate. The output of uric acid is low on the fat diet and increases on the addition of carbohydrate whilst the output of total creatinine is but little affected by the change of diet. Small amounts of creatine are excreted on a carbohydrate-free diet. The output of undetermined nitrogen is greater on diets containing carbohydrate than those from which carbohydrate is absent. S. S. Z.

**Constancy of the Creatine-Creatinine Excretion in Children on a High Protein Diet.** VICTOR JOHN HARDING and OLIVER HENRY GAEBLER (*J. Biol. Chem.*, 1922, **54**, 579—587).—The same amount of total creatine (creatine+creatinine) is excreted by normal children of the same age when under the same environment. The amount excreted per kg. of body weight ("total creatine coefficient") is constant for children of all ages and is of the same magnitude as the creatinine coefficient of an adult man. E. S.

**Elimination of Cholesterol in Urine.** WILHELM GRUNKE (*Biochem. Z.*, 1922, **132**, 543—555).—Cholesterol occurs in normal urine only in traces. In one case of icterus out of nine, 10.1 mg. per day was found, and in one case of diabetes out of five, 12.9 mg.; in other cases there was no more than a normal amount. W. O. K.

**Comparative Toxicity of Ammonium Salts.** FRANK P. UNDERHILL and ROBERT KAPSINOW (*J. Biol. Chem.*, 1922, **54**, 451—457).—From experiments on rats it is concluded that, in general, the toxicity of ammonium salts is directly proportional to their content of ammonia. E. S.

**Pharmacological Analogues of  $\alpha$ -2-Aminotetrahydronaphthalene.** JULIUS VON BRAUN, HEINRICH GRUBER, and GEORG KIRSCHBAUM (*Ber.*, 1922, **55**, [B], 3664—3674).—See this vol., i, 107.

## Chemistry of Vegetable Physiology and Agriculture

**Some Microbiological Consequences of the Oxidising Properties of Thorium-X.** P. LEMAY and L. JALOUSTRE (*Compt. rend.*, 1922, 175, 1053—1054; cf. A., 1922, ii, 13, 186).—In order to ascertain whether radioactive elements function as oxidation catalysts with regard to the activities of micro-organisms, cultures of anaërobic and aërobic organisms were submitted to the action of thorium-X. In the case of the anaërobic species (*Bacillus butyricus*) the radioactive material exercised an inhibiting effect on development, the number of bacteria being about one-twentieth and the gas evolved about one-third of that in the control experiment, whilst the action of the catalyst on the aërobic species (*B. lacticus*) appeared to be of a favourable nature. H. J. E.

**Influence of the Culture Conditions on the Liquefaction of Gelatin and on the Production of Indole by Bacteria.** OTTO ARNBECK (*Biochem. Z.*, 1922, 132, 457—479).—The production of indole and the liquefaction of gelatin by bacteria are inhibited by nitrogen-free foodstuffs such as glucose. Free ammonia, on the other hand, assists the liquefaction. W. O. K.

**Ultra-violet Absorption Spectra of some Vitaminic Extracts.** HORACIO DAMIANOVICH (*Anal. Asoc. Quím. Argentina*, 1922, 10, 209—214).—Yeast extracts containing vitamin-B show characteristic absorption spectra in the ultra-violet with general absorption in the extreme portion of the spectrum, and a band between 2478 and 2660 Å. which appears to be due to a pyrimidine or purine group. The absorption spectra of the oils from white and yellow maize, respectively, were also studied and a difference observed corresponding with the presence of vitamin-A in yellow maize oil and its absence from white maize oil. It is uncertain whether there is a causal connexion between presence of pigment and presence of vitamin-A in the yellow maize oil. Photospectrographs of the liquids examined are appended. G. W. R.

**Synthesis of Water-soluble [Vitamin]-B by Yeast Grown in Solutions of Purified Nutrients.** MARGARET B. McDONALD (*J. Biol. Chem.*, 1922, 54, 243—248).—Using five different varieties of yeast, the author confirms the conclusion of Nelson, Fulmer, and Cessna (A., 1921, i, 386) that this organism is able to synthesise vitamin-B. E. S.

**Vitamin-D.** TREVOR BRABY HEATON (*Biochem. J.*, 1922, 16, 800—808).—The activating substance of minimal concentrations of yeast (called by Wildiers "bios" and by Funk vitamin-D) is not identical with vitamin-B. Organs of pigeons rendered polynuritic contain it in the same amount as those of normal pigeons. Its distribution differs from that of antineuric vitamin. Rats subsisting on a diet deficient in the water-soluble vitamin incur also the deficiency of this activating substance. S. S. Z.

**Influence of Amines on Fermentation.** JULIUS ORIENT (*Biochem. Z.*, 1922, 132, 352—361).—The various amines used show in general a retarding effect on fermentation by yeast when applied in a concentration of 4·8%. This effect, however, changes into one of acceleration if the concentration of the amine be either higher or lower, except in the cases of methylamine and betaine which inhibit the fermentation even in low concentrations.

W. O. K.

**Fermentation of Sugar in Presence of Sodium Sulphite following Neuberg and Reinfurth. Equivalence between Aldehyde and Glycerol.** HEINRICH GEHLE (*Biochem. Z.*, 1922, 132, 566—588).—In the fermentation of sucrose by yeast in the presence of sodium sulphite there is in general rather more than one equivalent of glycerol formed for one equivalent of acetaldehyde. This is particularly the case with small amounts of sulphite, and a short fermentation time. As increased proportions of sulphite are used, the rate of increase in the yields of glycerol and of acetaldehyde gradually decreases until the maximum yield obtained using 60% of sulphite calculated on the sugar. With increasing percentage of sulphite, the rate of evolution of carbon dioxide is decreased.

W. O. K.

**Equivalence in the Production of Acetaldehyde and Glycerol at the Second Form of Fermentation.** C. NEUBERG, J. HIRSCH, and E. REINFURTH (*Biochem. Z.*, 1922, 132, 589—596).—Gehle's results (preceding abstract) are vitiated by a systematic error in the estimation of the acetaldehyde. If this be estimated gravimetrically by the "dimedon" method (A., 1920, i, 914), precise equivalence between glycerol and acetaldehyde is found.

W. O. K.

**The Chemistry of Fermentative Phenomena.** CARL NEUBERG (*Ber.*, 1922, 55, [B], 3624—3658).—A lecture delivered at the centenary of the Versammlung Deutscher Naturforscher und Aerzte.

H. W.

**The Presence of Urease and Urea in Fungi.** A. GORIS and P. COSTY (*Compt. rend.*, 1922, 175, 998—999; cf. A., 1922, i, 1220).—The distribution of urease in the pileus, stipe, and hymenium of twelve species of fungi was investigated. In all cases the hymenium contains the greatest proportion of the ferment. A brief account of the method of extraction and estimation of the urease is given.

H. J. E.

**The Action of the Nitrogen of Hexamethylenetetramine on Plant Growth.** E. BLANCH, W. GEHMANN, and F. GIESECKE (*J. Landw.*, 1922, 70, 221—251).—Pot experiments are described, which show that hexamethylenetetramine is as effective a fertiliser as ammonium sulphate. The soil bacteria decompose the substance into ammonia, which is nitrified in the usual way. The presence of hexamethylenetetramine in liquid farmyard manure, preserved by the addition of formaldehyde, brings no unfavourable consequences.

A. G. P.

**The Effect of the Kations of Salts on the Destruction and Synthesis of Starch in Plants.** W. S. ILJIN (*Biochem. Z.*, 1922, 132, 494—510).—The rate of disappearance of starch from plant cells immersed in a solution of a salt is influenced by the kation of the salt. Univalent kations and also barium and glucinum effect the solution of the starch and at the same time cause an increase of the osmotic pressure in the cell, whilst magnesium, calcium, and strontium are inactive. If, on the other hand, the cells be immersed in a solution of maltose the synthesis of starch is inhibited by the presence of barium, caesium, lithium, sodium, calcium, potassium, rubidium, magnesium, and strontium in order of decreasing activity.

W. O. K.

**Synthesis and Hydrolysis of Starch under the Influence of Anions in Plants.** W. S. ILJIN (*Biochem. Z.*, 1922, 132, 511—525; cf. preceding abstract).—Similar results are obtained with anions, the organic anions being particularly active in raising the osmotic pressure and influencing the synthesis and hydrolysis of starch.

W. O. K.

**Physiological Protection in Plants against the Harmful Action of Salts.** W. S. ILJIN (*Biochem. Z.*, 1922, 132, 526—542; cf. preceding abstracts).—The salt effects described in the preceding two abstracts would be harmful to plants, but it appears that certain ions act antagonistically to each other. Calcium, for instance, may inhibit the effect of sodium. In this way, the existence of halophytes may be understood.

W. O. K.

**Pigments of the Mendelian Colour Types in Maize: iso-Quercitrin from Brown-husked Maize.** CHARLES E. SANDO and H. H. BARTLETT (*J. Biol. Chem.*, 1922, 54, 629—645).—iso-Quercitrin has been isolated from the husks of a brown-husked maize. It forms primrose-yellow, needle-like plates, m. p. 220—222.5°, and is probably identical with the ragweed glucoside obtained by Heyl (A., 1919, i, 615). Aqueous solutions of iso-quercitrin give an olive-green coloration with ferric chloride, a yellow precipitate with lead acetate, and a rose-red colour on reduction with magnesium and hydrochloric acid. The yellow colour of the substance is intensified by sodium carbonate and dilute ammonia. The spectral transmission curves of both iso-quercitrin and quercetin have been determined.

E. S.

**Biological Adsorption from Solutions of Metallic Salts.** FRIEDRICH PICHLER and ARTUR WÖBER (*Biochem. Z.*, 1922, 132, 420—438).—An investigation of the adsorption particularly of copper and also of mercury and cerium from solutions of their salts, by the spores of maize rust (?) (*Maisbrandsporen*). In general there is a connexion between the degree of adsorption and the toxicity of the ion.

W. O. K.

## Organic Chemistry.

**New System for the Linear Representation of the Structure of all Organic Compounds.** T. SHERLOCK WHEELER (*Chem. News*, 1923, 126, 33—35, 49—50, 66—67).—A system designed to enable the structure of all organic compounds to be represented linearly by a simple arrangement of letters and figures, from which, with the aid of a few rules, the graphical formula could be deduced easily. The original must be consulted, as the paper does not end itself to abstraction.

**The Solubility of Methane in Water and Organic Solvents under Pressure.** F. FISCHER and C. ZERBE (*Brennstoff-Chem.*, 1922, iv, 17—19).—The solubility of mine gases of the composition methane 79.4%, carbon dioxide 0.7%, oxygen 2.8%, and nitrogen 17.1% in a large number of solvents under a pressure of about 10 atm., and also the composition of the gases evolved from the solvent were determined. The latter in most cases differed little from that of the original mixture, so that the figures obtained may be taken as approximately true for pure methane. The figure for the solubility in water (0.09 c.c. per g. for 1 atm.) is, however, so high owing to the higher solubility of carbon dioxide. The highest figure obtained is 1.34 for light petroleum (b. p. below 65°) others include: for ethyl alcohol 0.60, for chloroform 0.32, for niline 0.16. If the product of these solubility figures and the surface tension of the solvent are calculated, a series of figures which approximate to a constant is obtained as previously shown by Christoff for carbon monoxide. Water, nitrobenzene, aniline, and chloroform are exceptions. Both surface tension and solubility, however, decrease with a rise in temperature, and it is questionable whether a fair comparison is obtained at a uniform temperature (20°) between liquids of widely differing b. p. C. I.

**The Constituents of the Fraction of a Borneo Petroleum which Distills between 37° and 81°.** G. CHAVANNE (*Bull. Soc. Chim. Belg.*, 1922, 31, 331—364).—An examination of the petrol showed that all the possible isomerides of hexane are present, as are all the hydrocarbons derived from cyclopentane and cyclohexane the boiling points of which are included in the fraction investigated. With the exception of ethylcyclobutane, all the cyclic compounds present are derived from five- or six-membered rings. Of the hexanes present, normal hexane is the most abundant, followed by isohexane and  $\gamma$ -methylpentane, whilst  $\beta\beta$ -dimethylbutane and  $\beta\gamma$ -dimethylbutane are present in much smaller proportion. The saturated cyclic hydrocarbons present in quantity are cyclohexane and methylcyclopentane. A number of physical constants are given which differ slightly, if at all, from those in the literature, and the author states that the critical

temperature of solution in aniline (cf. Chavanne and Simon, A., 1919, ii, 267, 432, 433) and the density are important factors in the experimental study of complex mixtures of hydrocarbons (cf. Chavanne and Simon, A., 1919, i, 380). H. J. E.

**The Mechanism of Thermal Decomposition of the Pentanes**  
G. CALINGAERT (*J. Amer. Chem. Soc.*, 1923, 45, 130—135).—

When pentane vapour is passed through a tube at 600°, it is decomposed, giving hydrogen and a mixture of hydrocarbons. Under the experimental conditions, about 30% of the pentane is decomposed and 44% of the product consists of unsaturated hydrocarbons. The product contains hydrogen 5%, methane 12%, ethane 26%, propane 10%, pentane 4%, ethylene 10%, propylene 24%, butylene 3%, and 6% of a  $C_4H_6$  hydrocarbon. These results correspond with a rupture of the pentane molecule at the central carbon atom, giving an ethyl and a propyl group, one of which is then saturated at the expense of the other, which becomes unsaturated, the change going mainly in the direction of forming ethane and propylene. Under similar conditions, isopentane is also decomposed and an analysis of the products shows that in this case the molecule breaks on one side or the other of the tertiary carbon atom. This results in a methyl and an isobutyl group which give methane and  $\Delta^1$ - or  $\Delta^2$ -butylene. A second reaction gives an ethyl and an isopropyl group and ethane results, but never propane. There is also another reaction which occurs to a small extent and results in the formation of amylene, and, finally, a part of the amylene and butylene give, by a secondary reaction, butadiene and pentadiene. W. G.

**Constitution of Squalene.** RIKO MAJIMA and BENNOSUKÉ KUBOTA (*Japan. J. Chem.*, 1922, i, 19—33).—An English translation of the paper previously published in Japanese (this vol., i, 1). K. K.

**Preparation of Methyl Bromide.** ARTUR BYGDÉN (*J. pr. Chem.*, 1922, [ii], 104, 285—288).—Steinkopf and Schwen (A., 1921, i, 841) have obtained a 77% yield of methyl bromide, calculated on the bromine taken, if the reagents are employed in the ratio of 1 atom Br+0.5 atom P+2.5 mol. MeOH. It is now shown (cf. A., 1911, i, 43; also Holt, T., 1916, 109, 1) that a 97.3% yield may be obtained by using the following molecular proportions:  $1KBr:3H_2SO_4:2MeOH$ , the acid being diluted with one-third its weight of water previously to the addition of the other reagents. The most economical preparation, considering the cost of all the materials, is, however, effected by the use of  $1KBr:3H_2SO_4:1.25MeOH$ , the yield being then 95.9%. W. S. N.

**The Spontaneous Decomposition of Unsaturated Aliphatic Iodochlorides.** LLOYD B. HOWELL (*J. Amer. Chem. Soc.*, 1923, 45, 182—187; cf. Noyes, A., 1920, i, 469).—When  $\beta$ -chloroethylenic iodochloride decomposes spontaneously the products are iodine

monochloride, trichloroiodoethane,  $\alpha\beta\beta$ -tetrachloroethane, and  $\alpha$ -iodochloroiodoethane, and of these the first two are formed in much larger amounts than the last two. Under similar conditions,  $\beta$ -dichloro- $\beta$ -iodoethylene iodochloride gives no saturated compound except hexachloroethane. The principal products in this case are iodine monochloride and dichlorodi-iodoethylene, together with some  $\alpha$ -chloro- $\alpha\beta\beta$ -tri-iodoethylene and some trichloroiodoethylene. The changes consist in several rearrangements involving the splitting off of chlorine and iodine monochloride from the iodochloride group, the addition of one molecule of iodine monochloride or of chlorine to the unsaturated residues, and the replacement of iodine by chlorine or vice versa. If the carbon atoms of the double union in an unsaturated aliphatic  $\alpha$ -iodochloride hold hydrogen atoms, the products of its decomposition are saturated halogen derivatives, but if they hold only halogen atoms, the decomposition leads to unsaturated products. Compounds described are:  $\alpha\beta\beta$ -trichloro- $\alpha$ -iodoethane, b. p.  $101-102^\circ/31-32$  mm.,  $d_4^{25}$  2.266,  $n_D^{25}$  1.5834; (1)  $\alpha\alpha$ -dichloro- $\beta$ -iodoethane, b. p.  $146-148^\circ/28$  mm.,  $d_4^{25}$  2.861;  $\alpha\beta$ -dichloro- $\alpha\beta$ -di-iodoethylene, b. p.  $243.4^\circ$ , m. p.  $2.5-3.0^\circ$ ,  $d_4^{25}$  2.934; and  $\alpha$ -chloro- $\alpha\beta\beta$ -tri-iodoethylene.

W. G.

**Synthesis by Means of Magnesium Allyl Halides.** SAMUEL JOFFEY (*Rec. trav. chim.*, 1922, 41, 652-654).—A repetition of Jaworsky's preparation of allyldimethylcarbinol (A., 1909, i, 151) showed that dimethylallylcarbinyl allyl ether,  $C_3H_5 \cdot CMe_2 \cdot O \cdot C_3H_5$ , is obtained as a by-product, the yield being about 20%, calculated on the basis of the allyl chloride used. It is a pale yellow, mobile oil, b. p.  $190-193^\circ$ ,  $d_4^{25}$  0.8765,  $d_4^{20}$  0.8754,  $n_D^{25}$  1.4750. Dimethylallylcarbinol has m. p.  $-73^\circ$ ,  $d_4^{25}$  0.83553,  $d_4^{20}$  0.83452,  $n_D^{25}$  1.430. The acetate, obtained in 40% yield by modifying Houben's method (A., 1906, i, 520), has m. p.  $-94.5^\circ$ , b. p.  $46-48^\circ/21$  mm., or  $136-138^\circ$ /atmospheric pressure (decomp.),  $d_4^{25}$  0.88797,  $d_4^{20}$  0.88720,  $n_D^{25}$  1.4230. Neither of these substances reacted with solutions of perbenzoic acid.

H. J. E.

**The Oxidation of Propylene Glycol with Potassium Permanganate.** WILLIAM LLOYD EVANS (*J. Amer. Chem. Soc.*, 1923, 45, 171-176; cf. A., 1912, i, 743).—A study of the oxidation of propylene glycol by potassium permanganate at  $50^\circ$  and  $75^\circ$  in the presence of various concentrations of alkali. In neutral solutions, the products are acetic acid and carbon dioxide, but above certain minimum concentrations of alkali, oxalic acid is also an oxidation product. Rise in temperature causes an increase in the production of carbon dioxide and a decrease in the acetic acid. Lactic and pyruvic acids are probably two of the intermediate products, the lactic acid arising either from the oxidation of lactaldehyde or from the rearrangement of pyruvaldehyde in the presence of alkalis. The acetic acid is probably obtained either from the oxidation of acetaldehyde, present as a dissociation product, or from the oxidation of pyruvic acid. The oxalic acid is probably formed ( $\alpha$ ) by the oxidation of glycollic acid obtained

h 2

by the oxidation of vinyl alcohol, or (b) by the oxidation of glyoxylic acid, formed from pyruvic acid. Carbon dioxide may arise from the oxidation of formaldehyde, pyruvic acid, or glyoxylic acid. The alkali functions (a) by neutralising the acids formed, (b) by increasing the enolisation of acetaldehyde and pyruvic acid, (c) by causing the rearrangement of pyruvaldehyde to lactic acid. As the concentration of the alkali increases, the dissociation of the three-carbon atom compounds into two other compounds is suppressed in that direction, owing to the increased activity of the alcohol groups in propylene glycol, due to the lower point of dissociation of the alkyl oxides formed in comparison with that of the alcohol itself.

W. G.

**The Formation of Geometrical Isomerides by the Reduction of Acetylene Derivatives.** JUL. SALKIND (*Ber.*, 1923, 56, [B], 187—192).—It has been shown previously (A., 1907, i, 22) that  $\beta$ -dihydroxy- $\beta$ -dimethyl- $\Delta^7$ -hexinene,  $\text{OH}\cdot\text{CM}_2\cdot\text{C}:\text{C}\cdot\text{CM}_2\cdot\text{OH}$ , smoothly adds two atomic proportions of hydrogen in the presence of colloidal palladium and passes thereby into  $\beta$ -dihydroxy- $\beta$ -dimethyl- $\Delta^7$ -hexene,  $\text{OH}\cdot\text{CM}_2\cdot\text{CH}:\text{CH}\cdot\text{CM}_2\cdot\text{OH}$ , slender needles, m. p.  $76\cdot5$ — $77^\circ$  ( $\alpha$ -form). It has now been found possible to isolate the isomeric  $\beta$ -form, monoclinic prisms, m. p.  $69$ — $69\cdot5^\circ$ , the relationship of which to the  $\alpha$ -variety is established by the observation that either compound is smoothly hydrogenated in the presence of spongy platinum to tetramethylbutanediol. The  $\alpha$ - and  $\beta$ -forms are soluble to the extent of 0.55 and 5.14 parts in 100 parts of light petroleum ( $d$  0.64—0.66) at  $16^\circ$ . Either variety is transformed by bromine in the presence of carbon tetrachloride, carbon disulphide, or anhydrous ether into a mixture of the solid dibromide,  $\text{C}_8\text{H}_{16}\text{O}_2\text{Br}_2$ , long, thin prisms, m. p.  $98\cdot5$ — $99^\circ$ , and a liquid dibromide which could not be completely purified (the relative proportions of the solid and liquid products differ according to the isomeride used).

The author has endeavoured to elucidate the configuration of the glycols by a study of their conversion into the  $\gamma$ -oxide,  $\text{CH}\cdot\text{CM}_2\cdot\text{CH}\cdot\text{CM}_2\cdot\text{O}$  (a liquid, b. p.  $102$ — $102\cdot5^\circ/755$  mm.,  $d_4^{20}$  0.8226,  $n_D^{20}$  1.4093,  $n_D^{25}$  1.40926), which should be obtainable solely from the maleinoid form. Under the action of boiling sulphuric acid (15%), of potassium hydrogen sulphate at  $160^\circ$ , or of a trace of iodine, the oxide is, however, produced in good yield from either glycol, so that interconversion appears to take place under these conditions. Since, however, it is found that the  $\alpha$ -isomeride loses water much more readily than the  $\beta$ -form when heated under similar conditions with a little iodine, it is considered to be maleinoid in structure, whereas the fumaroid configuration is assigned to the  $\beta$ -form.

The relative proportion of the  $\alpha$ - and  $\beta$ -glycols obtained by hydrogenation of the acetylenic compound appears to depend on the rapidity of the action; the production of the  $\alpha$ -variety is favoured by the rapidity of the change.

H. W.

**The Cyclic Condensation Products of Acetone with 1:3-Diols.** J. BÖESEKEN [with G. SCHAEFER and P. HERMANS] (*Rec. trav. chim.*, 1922, **41**, 722—723; cf. Böeseken and van Loon, A., 1920, i, 837; Mannich and Brose, A., 1922, i, 1118).—Two condensation products of erythritol with acetone were prepared. *Acetone-erythritol* [erythritol isopropylidene ether] has m. p. 135° and is only slightly soluble in benzene. *Diacetone-erythritol* [erythritol diisopropylidene diether], m. p. 116°, is soluble in benzene. The solubility difference affords a means of separating the substances from each other. H. J. E.

**A New Preparation of Monochloroacetic Acid.** L. J. SIMON and G. CHAVANNE (*Compt. rend.*, 1923, **176**, 309—311).—Monochloroacetic acid may readily be prepared with a yield of 90% by heating trichloroethylene with 90—93% sulphuric acid at 160—180°. The concentration of the acid and the temperature are regulated so as to give the best yield and the greatest reaction velocity. Part of the chloroacetic acid passes over with the hydrochloric acid and unchanged trichloroethylene and a certain amount remains dissolved in the sulphuric acid. The latter may be recovered by distillation under reduced pressure or by diluting the acid and extracting it with ether. Its presence dissolved in the sulphuric acid does not prevent the further use of the acid as a hydrating agent after the addition of the necessary amount of water to replace that used in the first hydration. W. G.

**Hydroxystearic Acid and some of its Derivatives.** L. GUY RADCLIFFE and W. GIBSON (*J. Soc. Dyers and Col.*, 1923, **39**, 4—10).— $\alpha$ -Hydroxystearic acid prepared by the action of sulphuric acid on oleic acid (*ibid.*, 1920, **36**, 65) and purified by repeated crystallisation from alcohol, melted sharply at 85°. The acid was further characterised by the preparation of the following derivatives: *Methyl hydroxystearate*, small, white flakes, m. p. 46°; *ethyl hydroxystearate*, white flakes, m. p. 48.5°; *acetoxystearic acid*, a white powder, m. p. 31—32°; and *ethyl benzoxystearate*, a yellow oil. As an attempt to introduce the  $-\text{NO}_2$  group into the stearic acid molecule,  $\alpha$ -bromostearic acid was prepared by Volhard's method. It is a white substance, m. p. 58°, and gives with silver nitrate, in alcoholic solution, a product free from nitrogen which seemed to be a mixture of  $\alpha$ -hydroxy- and  $\alpha$ -ethoxy-stearic acids. By the direct action of fuming nitric acid in acetic acid solution on the original  $\alpha$ -hydroxystearic acid, three substances were obtained, a greenish-yellow, crystalline compound, m. p. 83—83.5°, a yellow oil, and a white solid, m. p. 100—120°. Only the first of these was further investigated. It was free from nitrogen, and had a molecular formula approximating to  $\text{C}_{18}\text{H}_{34}\text{O}_4$ . No confirmation of this could, however, be obtained by a molecular-weight determination. Titration with alcoholic potassium hydroxide in the cold and the analysis of the silver salt gave values of 291—293, but on warming with the alkali a further half molecule was neutralised, suggesting a lactonic structure. Still no confirmation

of this was forthcoming, neither was it in accord with the number of oxygen atoms found by the combustion. G. F. M.

**$\alpha\beta$ -Dihydroxynonoic Acid.** WALTER KROHS (*Ber. Deut. pharm. Ges.*, 1922, 32, 336—338; cf. Thoms and Deckert, A., 1921, i, 219; Reinger, A., 1922, i, 623).— $\alpha\beta$ -Dihydroxynonoic acid,  $\text{CH}_3\text{Me}[\text{CH}_2]_4\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$ , was obtained by the action of 2% potassium permanganate on the corresponding nonenoic acid (Harding and Weizmann, T., 1910, 97, 299) and has m. p.  $123^\circ$  (sinters at  $119^\circ$ ). Dehydrating agents, such as 60% sulphuric acid, do not convert it into an unsaturated substance, and with 60% sulphuric acid and 40% acetic acid a *monoacetyl* compound is formed. It is considered that the stability of the hydroxyl group to dehydrating agents is due to the proximity of the carboxyl group. The acid was resolved into its optical antipodes by means of cinchonine. The *l*-acid has  $[\alpha]_D^{20} -17.44^\circ$ ; the *dextro*-acid was not obtained quite pure. On further oxidation the acid easily decomposes, but a well characterised *dinitrate*,

$\text{CH}_3\text{Me}[\text{CH}_2]_4\text{CH}(\text{O}\cdot\text{NO}_2)\text{CH}(\text{O}\cdot\text{NO}_2)\text{CO}_2\text{H}$ , and  $\alpha\beta$ -diketononoic acid,  $\text{CH}_3\text{Me}[\text{CH}_2]_4\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , were obtained. The latter has m. p.  $95-96^\circ$ , and its *dihydrazone*, and *disemicarbazide*, m. p.  $160^\circ$ , were prepared. P. M.

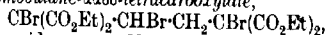
**Crystalline Structure and Properties of Tartaric Acid.** W. T. ASTBURY (*Proc. Roy. Soc.*, 1923, [A], 102, 506—528).—By X-ray analysis, employing a Coolidge bulb with molybdenum anticathode, the unit cell in the crystal structure of active tartaric acid has been shown to be monoclinic, to contain two molecules, and to have the following dimensions:  $a = 7.693 \text{ \AA}$ ,  $b = 6.037 \text{ \AA}$ , and  $c = 6.195 \text{ \AA}$ . Molecules at the corners of the cell point in one direction, whilst those lying along the central line of the cell parallel to the  $a$  axis point in a diametrically opposite direction. Intensity measurements of the reflections from various planes in the crystal enable the manner in which the unit cell is incorporated in the crystal structure to be ascertained, and hence the structure itself to be determined. This shows only one plane of perfect cleavage, viz., the plane about which lie the junctions of the hydroxyl groups, i.e., the plane (100). The junctions in the  $\text{—OH—}$  linkings are of a different type from the junctions between the hydrogens of the hydroxyl groups. In the main, the ascertained crystal structure is in accordance with known chemical and physical facts. The theory of stereoisomerism of Le Bel and van't Hoff is in its essentials confirmed, and the link between crystallographic enantiomorphs and the chemical stereoisomerides revealed. The rotatory properties of the acid are discussed with reference to the symmetry of the crystal and the spiral arrangement within the molecule, and it is shown that the assumption by Lowry of the existence of dynamic isomerides within the structure to explain these properties is unnecessary, the crystal structure itself affording a simple explanation of all the facts. Thus the fundamental crystal cell is constructed of molecules exhibiting

two spiral arrangements, one associated with the four carbon atoms forming the nucleus of each molecule, and one, oppositely directed, associated with the four hydroxyl groups. In these spiral formations are located the two opposing rotatory systems adequate to explain the anomalous rotatory properties of the acid and some of its derivatives. Most probably the dextro-rotatory property of ordinary tartaric acid is associated with the carbon nucleus of the molecule. It is shown to be impossible by the diffraction of X-rays to discriminate between the dextro- and levo-forms of an optically active substance. J. S. G. T.

**Some Complex Organic Compounds of Bismuth.** E. MOLES and R. PORTILLO (*Anal. Fis. Quím.*, 1922, 20, 571—576).—Preliminary data are given on the preparation and properties of bismuthotartaric acid, bismutholactic acid, and bismuthocitric acid. G. W. R.

**A Synthesis of Derivatives of Muconic Acid.** ERICH BENARY and RUDOLF SCHINKOPF (*Ber.*, 1923, 56, [B], 354—362).—The synthesis depends on the action of  $\alpha\beta$ -dichloroethyl ether,  $\text{CH}_3\text{CH}(\text{CHCl})\text{OEt}$ , on ethyl sodiomalonate.

$\alpha\beta$ -Dichloroethyl ether is added gradually to a suspension of ethyl sodiomalonate in boiling ether; after removal of a fraction containing chloroacetaldehyde, chloroacetal, unchanged dichloroethyl ether, and malonic ester, ethyl  $\Delta^4$ -butene- $\alpha\alpha\delta\delta$ -tetracarboxylate,  $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , is isolated as a colourless, viscous liquid, b. p. 223—225°/13 mm. (some decomp.). It is reduced by zinc dust and boiling glacial acetic acid to ethyl butane- $\alpha\alpha\delta\delta$ -tetracarboxylate (cf. Perkin, T., 1894, 65, 579). It is converted by cold saturated alcoholic ammonia at the atmospheric temperature into the corresponding triamide,  $\text{C}_{10}\text{H}_{15}\text{O}_5\text{N}_3$ , small needles, m. p. 230° (decomp.), and by concentrated aqueous ammonia into the tetra-amide,  $\text{C}_8\text{H}_{12}\text{O}_4\text{N}_4$ , small, colourless needles, m. p. 257° (decomp.) after incipient change at 238°. Hydrolysis of the ester with alcoholic potassium hydroxide solution and subsequent addition of lead acetate leads to the production of the salt,  $\text{C}_{10}\text{H}_{10}\text{O}_{16}\text{Pb}_3$ , which seems to be derived from a tribasic acid; the latter is an amorphous, brittle, colourless mass. The unsaturated ester is converted by bromine in the presence of chloroform in ethyl  $\alpha\beta\delta$ -tribromobutane- $\alpha\alpha\delta\delta$ -tetracarboxylate,



hexagonal pyramids, m. p. 61—63°, which, when distilled under diminished pressure or warmed with pyridine, passes into ethyl  $\Delta^4$ -butadiene- $\alpha\alpha\delta\delta$ -tetracarboxylate,  $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , colourless, matted needles, m. p. 56—57°. The latter substance is reduced by zinc dust and glacial acetic acid to ethyl butane- $\alpha\alpha\delta\delta$ -tetracarboxylate. The ester is converted by fuming hydrochloric acid into a mixture of  $\beta\gamma$ -diethoxy-n-butane- $\alpha\alpha\delta\delta$ -tetracarboxylic acid, colourless needles, m. p. 132°, which evolve carbon dioxide at about 140°, and  $\beta\gamma$ -diethoxy-n-butane- $\alpha\delta$ -dicarboxylic acid, crystalline scales, m. p. 19·5°, b. p. 149°/13 mm. The latter

acid is converted by bromine in the presence of chloroform into *α,δ*-dibromo- $\beta$ - $\gamma$ -di( $\alpha$ ' $\beta$ '-dibromoethoxy)adipic acid,  
 $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CH}(\text{O}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br})\cdot\text{CH}(\text{O}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br})\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ ,  
 small, colourless needles, m. p. 77–78°.

The condensation of an excess of  $\alpha\beta$ -dichloroethyl ether with an ethereal suspension of ethyl sodiomalonate at a low temperature leads to the production of *ethyl β-chloro-α-ethoxyethylmalonate*,  
 $\text{CH}_3\text{Cl}\cdot\text{CH}(\text{OEt})\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , a colourless, mobile liquid, b. p. 149–152°/13 mm. H. W.

**Selective Hydrogenation.** THOMAS PERCY HILDITCH and CHARLES WATSON MOORE (*J. Soc. Chem. Ind.*, 1923, 42, 15–17).—Conclusive proof of the preferential saturation of one or more double bonds in the catalytic hydrogenation of compounds containing several unsaturated linkings is furnished by a study of the hydrogenation of a number of natural oils and of the esters prepared from their fatty acids. Samples were withdrawn at intervals corresponding with a drop of 10–20 in the iodine value, and the proportion of saturated and unsaturated fatty acids and of oleic to linoleic acid was calculated from the iodine values obtained. It was found that the amount of saturated derivatives present did not increase until the amount of linoleic derivatives had fallen to 10%, or even less, of the mixture. It is clear, therefore, that linolein and linolenin are almost completely hydrogenated to olein before the unsaturated centre in olein is affected. In the case of the free acids, the strong attraction between the free carboxyl group and the metal dwarfs to some extent the relative activities of the different unsaturated systems. G. F. M.

**Perilla Oil.** K. H. BAUER (*Chem. Umschau*, 1923, 30, 9–11; cf. A., 1922, i, 983).—The unsaturated acids obtained by debrominating the bromides soluble in a mixture of ether and glacial acetic acid were oxidised by Hazura's method with alkaline permanganate. The resulting mixture of hydroxy-acids was extracted successively with light petroleum, ether, and water. The light petroleum extract was a viscid, yellow oil, which slowly deposited a crystalline mass and was similar to the corresponding extract of the oxidation products of the total fatty acids from perilla oil. The crystalline deposit consisted of palmitic acid, and was due to the imperfect separation of saturated and unsaturated acids given by the lead salt-benzene method. The ethereal extract consisted of a white, crystalline mass of dihydroxystearic acid, m. p. 131°, and comprised 5.7% of the debrominated acids originally oxidised. Glycerides of oleic acid are therefore present in perilla oil. The aqueous extract comprised only 1.5% of the original acids oxidised, and its nature was not determined. Very small quantities of linusic and isolinusic acids were isolated from the insoluble residue. It appears from this that the linolenic acid from perilla oil gives the same hexabromostearic acid as that from linseed oil, but on oxidation of the former with alkaline permanganate, in addition to linusic and isolinusic acids, an isomeric hexahydroxystearic acid is obtained, which is not obtained from the linolenic acid from linseed oil.

The linolenic acid obtained by the debromination of hexabromo-stearic acid is, however, different from that originally brominated, and only yields 14% of its weight of insoluble bromides. It therefore appears that conclusions as to the presence or absence of isomeric linolenic acids cannot be based only on the behaviour on bromination.

H. C. R.

**The Equilibrium between Formaldehyde and Amino-acids in Aqueous Solution.** JULIUS SVEHLA (*Ber.*, 1923, 56, [B], 331—337).—The reaction between amino-acids and formaldehyde in dilute aqueous solution has been examined, and the corresponding equilibrium constants are calculated in accordance with the equation:  $C_{\text{Alk}} \times C_{\text{acid}} / C_{\text{Alk-acid}} = K$ . The following values are observed: glycine, 1.73; alanine, 14.1; valine, 28.9; leucine, 38.8; aspartic acid, 25.7; glutamic acid, 30.7. Leucylglycine appears to react with two molecular proportions of formaldehyde in dilute aqueous solution.

In the cases of the simpler amino-acids, the measurements are effected by determining the freezing points of solutions of the acid and formaldehyde singly and when mixed. With the more complex acids, the results are deduced from determinations of their solubility in pure water and in formaldehyde solutions of certain concentrations at 25°.

H. W.

**Action of Aldehydes on Mixtures of Sulphites and Hydrogen Sulphites.** J. ESTALELLA (*Anal. Fis. Quim.*, 1922, 20, 437—441).—When formaldehyde is added to a solution containing potassium sulphite and potassium hydrogen sulphite, the following reactions take place successively: (1)  $\text{H}\cdot\text{CHO} + \text{KHSO}_3 = \text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$  and (2)  $\text{H}\cdot\text{CHO} + \text{K}_2\text{SO}_3 + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K} + \text{KOH}$ . The gradual liberation of potassium hydroxide is demonstrated by the reddening of added phenolphthalein. A similar reaction is given by a solution of potassium sulphite alone in the presence of carbon dioxide, but the red colour with phenolphthalein is then non-persistent. It is suggested that the presence of carbon dioxide in the distillate may interfere with the estimation of volatile acid in wines.

G. W. R.

**Density and the Refractive Index of Mixtures of Acetaldehyde and Water or Ethyl Alcohol.** E. VAN AUBEL (*Bull. Acad. roy. Belg.*, 1921, 160—162).—Mainly a question of priority. Attention is also directed to some values for the coefficient of thermal expansion of certain mixtures of acetaldehyde and water.

E. E. T.

**Syntheses by Means of Mixed Organo-zinc Derivatives: Propylglyoxal.** E. E. BLAISE (*Compt. rend.*, 1922, 175, 1216—1218).—The action of oxalyl chloride on  $\alpha$ -hydroxyisobutyric acid yields oxalylbisoxoisobutyric acid. The dichloride of this acid on treatment with zinc propyl iodide forms a mixture of the bisoxalacetaloxyisobutyrate of dibutyl and of propylglyoxal. Alcoholysis of the mixture leaves the former substance unchanged, and decomposes the latter into ethyl hydroxyisobutyrate and the

h\*

acetal of propylglyoxal. The action of methyl alcohol on the mixture of acetals yields the *dimethylacetal* of *propylglyoxal*,  $C_5H_8CO\cdot CH(OMe)_2$ . This is a mobile, colourless liquid, b. p. 65–66°/14 mm., which forms a *disemicarbazone* crystallising from acetic acid with one molecule of the solvent, m. p. above 250°, and a *osazone*, yellow needles, m. p. 105°. On boiling with 3% sulphuric acid, hydrolysis takes place with liberation of *propylglyoxal*, a yellowish-green liquid, b. p. 36°/16 mm.; the vapour is of the same colour as the liquid. On being kept in a sealed tube, it becomes viscous and of paler colour; in air it is rapidly oxidised. It has a powerful reducing action and rapidly restores the colour of Schiff's reagent. H. J. E.

**The Nomenclature of Steric Series.** A. WOHL and K. FREUDENBERG (*Ber.*, 1923, 56, [B], 309–313).—In two almost simultaneous communications (Wohl, A., 1922, i, 626; Freudenberg, A., 1922, i, 623) systems of nomenclature of steric series have been proposed which differ from one another in certain details; in order to avoid confusion, the following system is advocated.

The direction of the rotation of a compound is indicated by prefixing the sign + or – to the name, thus (+)-glucose, or (+)-tartaric acid. This is the only possible system in the case of many substances, such as tannins and alkaloids, which cannot at present be brought into line with the stereochemical structure of the sugars. It is, however, open to the objection that it is not distinctive in cases in which the sign of rotation varies with the concentration (malic acid), or in which inversion occurs when the acid is converted into its salt (*e.g.*, glyceric acid).

The genetic relationship to glyceraldehyde is adopted as the determining factor in the nomenclature of hydroxy-acids and sugars. The *d*-form of the aldehyde is written as shown in the annexed formulae I and II. All compounds containing one asymmetric carbon atom which are genetically related to glyceraldehyde and in which the hydroxyl group is to the right of or below the asymmetric carbon atom belong to the *d*-series.

In the cases of compounds with several carbon atoms, each of the latter is indicated in the same manner; the system is distinctive for the sugars themselves and their unsymmetrical derivatives. If the carbonyl group is written at the top of or to the right of the formula, the position of the steric model is established, and also the configurative formula. The order of the single carbon atoms is from below to above or from left to right, because this sequence corresponds with the relation of the sugars to glyceraldehyde; (+)-glucose is thus designated *ddld*. [This necessitates an inversion of Fischer's symbols in the cases of gulose, idose, xylose, and threose, as proposed previously by Rosanoff (A., 1906, ii, 320).]

The mode of formulating symmetrical derivatives of the sugars according to this system is somewhat indefinite. Thus, saccharic

acid is lettered *dddd* if regarded as derived from glucose and *U* if considered as formed from gulonic. In such cases, it is recommended that the relationship to the more important sugar should be expressed, or, as this is arbitrary, that merely the sign of rotation should be given, (+)-saccharic acid. H. W.

**Optical Rotatory Power of Sugars in Hydrochloric Acid.** ISZLÓ ZECHMEISTER (*Z. physikal. Chem.*, 1922, 103, 316—336).—The optical rotation and its change with time has been determined at 0° and 10° in concentrated hydrochloric acid (40.6%) solutions at various concentrations of the following sugars: dextrose, alactose, mannose, arabinose, xylose, rhamnose, and lævulose. The results show that aldo-hexoses and aldo-pentoses in cold concentrated hydrochloric acid solution undergo a measurable reversible change which is evidenced by a large increase of the specific rotation to a constant end-value. The position of the end-value is determined by the concentration of the hydrochloric acid, and in highly concentrated acid exceeds the value of  $[\alpha]_D$  for the  $\alpha$ -form of the sugar in water solution. In the case of dextrose, in 46.7% hydrochloric acid the value of  $[\alpha]_D^{12}$  is +202°. Lævulose shows a somewhat irregular behaviour. Possibilities for the explanation of this phenomenon are considered. J. F. S.

**The Biochemical Synthesis of an  $\alpha$ -D-Mannoside Starting from Manna.** H. HÉRISSEY (*Compt. rend.*, 1922, 175, 1110—1112; cf. A., 1921, i, 628).—The action of dried and powdered cerise seeds [as a source of  $\alpha$ -D-mannosidase] on manna in presence of methyl alcohol results in the formation of  $\alpha$ -methyl-D-mannoside. The manna was not present in pure condition, but as carob seed (*Ceratonia siliqua*), which contains a considerable amount of the carbohydrate. The author suggests that in such a reaction the sugar may have at the moment of formation a different structure from that which it possesses in the crystalline form, and indicates the possibility of preparing glucosides directly from starch by a suitable choice of enzymes. H. J. E.

**The Constitution of the Disaccharides. VII. Sucrose.** WALTER NORMAN HAWORTH and WILFRED HERBERT LINNELL (*T.*, 1923, 123, 294—301).

**The Constitution of the Disaccharides. VIII. Sucrose.** WALTER NORMAN HAWORTH and JAMES GIBB MITCHELL (*T.*, 1923, 123, 301—310).

**Pentosans. III. Purity of Xylan from Straw Cellulose.** EMIL HEUSER and MARIA BRADEN (*J. pr. Chem.*, 1922, [ii], 104, 250—264).—It is shown that the lignin content of crude xylan, even if it contains methylxylan, may be estimated by Zeisel's method, but the method is a rough one only, since it depends on knowledge of the methoxyl content of lignin, in the isolation of which loss of methoxyl occurs (cf. Heuser and Wenzel, A., 1921, ii, 715). A sample of xylan prepared by the modified method of Salkowski (cf. A., 1903, i, 206) is in this way shown not to contain

lignin; the absence of methyl pentosan is demonstrated by the method of Tollens and Ellet (A., 1905, ii, 210).

By a modification of Schulze's process (*Z. physiol. Chem.*, 1892, 16, 403) xylan is prepared from bleached straw cellulose, in 19% yield, containing 93.8% of pure xylan and 0.94% of ash. Precipitation of xylan by calcium chloride solution from a nearly neutralised alkaline solution, and further purification by dialysis, gives a product containing 12.2% of ash, corresponding with a yield of 22% of ash-free xylan. Further purification by solution in sodium hydroxide solution and reprecipitation with acid reduces the ash content to 0.6%, but the yield is then only 15%. These results compare unfavourably with those obtained by the more expensive Salkowski method.

W. S. N.

**Pentosans. IV. Hydrolysis of Xylan by Dilute Acids.** EMIL HEUSER and LUDWIG BRUNNER (*J. pr. Chem.*, 1922, [ii], 104, 264—281).—It is shown that when xylan is hydrolysed by means of hot hydrochloric acid solution (5% or 12%) or by hot dilute sulphuric acid (12%), the xylose produced is partly converted into humin-like substances before the parallel conversion into furfuraldehyde commences; if, however, the hydrolysis is continued, the formation of furfuraldehyde is mainly accountable for the loss of xylose. The course of the hydrolysis is followed by a method already described (Heuser and Kürschner, A., 1922, i, 113).

W. S. N.

**Acetyl Derivatives of Xylan.** EMIL HEUSER and PAUL SCHLOSSER (*Ber.*, 1923, 56, [B], 392—395).—The presence of two free hydroxyl groups in xylan, established previously by the production of a dimethyl derivative (Heuser and Ruppel, A., 1922, i, 810) is confirmed by the isolation of a diacetate.

The treatment of xylan with boiling acetic anhydride or with acetyl chloride at the atmospheric temperature does not yield a completely acetylated product, since the acetates are to some extent hydrolysed by the acetic or hydrochloric acid produced simultaneously. This action can be limited by the addition of pyridine, and under these conditions the diacetate, a colourless powder, is obtained in 90% yield. Unlike cellulose, therefore, xylan may be acetylated in the absence of a catalyst, but the experimental conditions can be made less drastic if such an agent is present. The most suitable substance for this purpose is concentrated nitric acid; sulphuric acid is objectionable on account of its tendency to yield charred products. Dry, powdered xylan reacts with difficulty, but can be brought into a more suitable condition by allowing it to swell in water and removing the latter by treating the product successively with acetic acid and acetic anhydride.

H. W.

**Cellulose Chemistry. II. The Action of Dry Hydrogen Bromide on Carbohydrates and Polysaccharides.** HAROLD HIBBERT and HAROLD S. HILL (*J. Amer. Chem. Soc.*, 1923, 45, 176—182; cf. *J. Ind. Eng. Chem.*, 1921, 13, 256, 334).—The authors have repeated the work of Fenton and Gostling (T., 1898,

73, 554; 1899, 75, 423; 1901, 79, 361; 1909, 95, 1334) on the action of dry hydrogen bromide on carbohydrates and polysaccharides. Contrary to the results of these workers, a yield of 12% of  $\omega$ -bromomethylfurfuraldehyde was obtained from pure dextrose, from  $\alpha$ -methylglucoside the yield was 15%, and from cellobiose 27%. In one case, from a dry cotton cellulose, a 56% yield was obtained. The formation of  $\omega$ -bromomethylfurfuraldehyde under these conditions is not, therefore, alone characteristic of ketoses and ketose derivatives, but also takes place with aldoses and related compounds. Its formation from cellulose is thus no criterion as to the presence of ketone groupings in this product (cf. Cross and Bevan, "Cellulose," 1918). W. G.

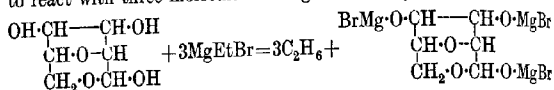
**Chemical Decomposition of Cellulose by Oxidation under Pressure.** FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 211—220; from *Chem. Zentr.*, 1922, iii, 1185).—By oxidation of cellulose in sodium carbonate solution under pressure at 200°, 42% of the material used is obtained as acids. Of these, about 11% consists of oxalic acid, and more than 50% of acetic acid. About 25% (9% of the original cellulose) consists of non-volatile acids extractable with ether: these include fumaric acid and succinic acid. Small amounts of formaldehyde are also obtained. On heating cellulose under pressure, both hydrolysis and oxidation take place. Sugars may be formed which undergo oxidation. G. W. R.

[Effect of] **Heating under Pressure of Alkaline Solutions obtained from the Oxidation under Pressure of Cellulose and Lignin.** FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 311—318; from *Chem. Zentr.*, 1922, iii, 1186).—By heating the solution of sodium salts, obtained by heating 100 g. of dry cellulose at 200° in the presence of sodium carbonate solution, at 400° under pressure, the following were obtained: gases, 6.5 litres; oils, 1.5 g.; tarry substances, 2.7 g.; volatile acids (acetic and formic acids), 0.28 equivalent; ether acids, 1.2 g. (0.014 equivalent). Similarly treated, 100 g. of lignin gave: gases, 3.4 litres; oil, 1.6 g.; volatile acids, 0.17 equivalent (including benzoic acid, 0.7 g.); humic acids, 2.0 g.; sphthalic acid, 1.8 g.; acids extractable by ether, 1.1 g. G. W. R.

[Effect of] **Heating Cellulose and Lignin under Pressure in the Presence of Water and Aqueous Alkalis.** FRANZ FISCHER and HANS SCHRADER (*Ges. Abh. Kennt. Kohle*, 1921, 5, 332—359; from *Chem. Zentr.*, 1922, iii, 1184—1185).—Cellulose is increasingly decomposed with rising temperature when heated under pressure in the presence of water, giving compounds, including acids, soluble in water, and gaseous products, principally carbon dioxide, and some hydrogen; comparatively little solid residue remains. Decomposition takes place slowly at 200°, but more completely at 300°. Lignin also gives carbon dioxide, but the principal product is black carbonaceous material. Sulphite liquors, heated at 300°,

give insoluble substances which are precipitated as a black powder. Probably association to larger molecules takes place. Cellulose in the presence of alkalis is more resistant than lignin when heated under pressure at 200°. At 300°, strong decomposition takes place with evolution of carbon dioxide and formation of small amounts of an oil of powerful odour together with formic acid, acetic acid, and other decomposition products. Lignin, heated under pressure with aqueous alkalis, goes completely into solution at 200°, with formation of humic substances. On heating the dark brown solution at 300°, the humic acids associate and separate as dark brown or black masses. Wood, peat, bituminous coal, and anthracite heated under pressure with potassium hydroxide solution behave according to their composition. G. W. R.

**Magnesyl Derivative of Cellulose.** D. COSTA (*Gazzetta*, 1922, 52, ii, 362—365).—On the basis of Green's formula for cellulose, the latter, in virtue of its three hydroxyl groups, might be expected to react with three molecules of magnesium ethyl bromide:



The author finds that, at a temperature not exceeding 35°, an ethereal solution of magnesium ethyl bromide acts on cellulose, yielding ethane and a greenish-grey compound which shows the fibrous structure of the original cellulose and has the composition of a *magnesium cellulose bromide*,  $\text{C}_6\text{H}_7\text{O}_5\cdot\text{MgBr}\cdot\text{Et}_2\text{O}$ . This compound reacts with avidity with water, giving cellulose and magnesium bromohydroxide. It was not found possible to introduce more than the one bromomagnesium residue into the cellulose molecule. T. H. P.

[**Cellulose Copper Compounds.**] WILHELM TRAUBE (*Ber.*, 1923, 56, [B], 268—274).—Hess and Messmer's conception (*A.*, 1921, i, 401; 1922, i, 988) of the constitution of the compounds formed by the solution of cellulose in copper oxide-amine solutions is identical in its essential features with that previously put forward by Traube (*A.*, 1922, i, 115, 718). In the author's opinion, the electrolytic observations of Hess and Messmer (*loc. cit.*) do not justify the conclusions which they have based on them and an alternative interpretation of the results is given. H. W.

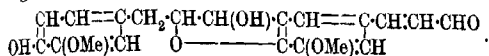
**Physico-chemical Studies of Cellulose Nitrates in Organic Media.** I and II. J. NEWTON KUGELMASS (*Rec. trav. chim.*, 1922, 41, 751—754, 755—763).—A study of the physical properties of solutions of cellulose nitrate (nitrogen content 11.9%) in ether and in alcohol prepared at a low temperature. Estimation of the nitrogen content of the solute in each case (11.20% and 14.02% respectively) showed that the ethereal solution apparently contains cellulose dinitrate, whilst the constituent soluble in alcohol is the trinitrate. The viscosity of the ethereal solution compared with that of the pure solvent is greater at temperatures

below  $-20^{\circ}$  but identical above this point, the maximum difference observed being in the neighbourhood of  $-90^{\circ}$ . Other properties of the ethereal solution are similar to those of aqueous solutions of colloids.

H. J. E.

**Constitution of Pine Lignin. III.** PETER KLASON (*Ber.*, 1923, 56, [B], 300—308; cf. *A.*, 1920, i, 822; 1922, i, 324).—The preparation of  $\beta$ -lignosulphonic acid and of its  $\beta$ -naphthylamine and calcium salts is described. New analyses lead to the formula  $C_{19}H_{18}O_6$  for  $\beta$ -lignin in place of  $C_{19}H_{18}O_5$  proposed previously (*A.*, 1920, i, 822). The calcium salt is converted by molten potassium hydroxide into protocatechuic acid.

$\alpha$ -Lignin is regarded as formed by the condensation of two molecules of coniferyl aldehyde in such a manner that two hydrogen atoms have undergone change in position and the annexed formula is assigned to it:



In this formula, the skeletons of guaiacol, pyrocatechol, *m*- and *p*-cresols, and methyl-, ethyl-, and *n*-propyl-cresols are present, and all these substances are present in pine tar. The formation of methyl alcohol, allyl alcohol, and 2-methylfuran is also explained.

Attempts are described to effect the synthesis of coniferyl aldehyde by the condensation of vanillin with acetaldehyde in dilute aqueous solution in the presence of sodium hydroxide. In place of the desired compound, however, its dimeric form is obtained, which, in virtue of the aldehyde group, can react with one molecular proportion of sulphite, but is distinguished from acraldehyde-lignin by its inability to combine with a second molecular proportion of sulphite as a consequence of the presence of the double bond.  $\alpha$ -Lignin, however, after very mild treatment with calcium hydroxide, loses the ability to become converted into  $\alpha$ -lignosulphonic acid. It is considered that the synthetic dimeric coniferyl alcohol is identical with hemi- $\alpha$ -lignin.

Further attempts to prepare coniferyl aldehyde by the regulated oxidation of coniferin did not lead to the desired result, the dimeric form being again obtained.

A condensation product,  $C_{30}H_{27}O_5N$ , from vanillin and  $\beta$ -naphthylamine is incidentally described.

H. W.

**Chemical Decomposition of Lignin by Oxidation under Pressure.** FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 221—229; from *Chem. Zentr.*, 1922, iii, 1185).—Lignin, prepared by treatment of wood with concentrated hydrochloric acid (Willstätter and Zechmeister), contains 60.6% of carbon, 4.5% of hydrogen, 12.6% of water, and 3.3% of ash. When shaken with 2.5*N*-sodium carbonate solution in the presence of air at  $200^{\circ}$ , a dark coloured solution is obtained, 44% of the lignin remaining undissolved, a total of 0.101 equivalent of acid being obtained of which 0.0185 is volatile in steam. Carbon

dioxide, equivalent to 8.4% carbon, 0.60% of a neutral oil, 9.6% of humic acids, and 4.2% of ether-soluble non-volatile acids are also obtained. By oxidation for forty hours, 0.55 equivalent of acids (including 0.18 equivalent volatile in steam, and 0.16 equivalent of oxalic acid), 18.9% of non-volatile acids (by extraction with ether), 0.31% of mellitic acid, and 4.2% of water soluble calcium salts were formed.

G. W. R.

[Effect of] Oxidation and Heating under Pressure of Humic Substances from Sucrose. FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 230—234; from *Chem. Zentr.*, 1922, iii, 1186).—Humic substances obtained by the method of Conrad and Guthzeit were submitted to oxidation under pressure at 200° for eight and three-quarter hours. 2.2 Equivalents of acid were thus formed: the solution obtained was clear and reddish-brown. After acidifying, 0.27 equivalent of volatile acid (acetic acid) was obtained by steam distillation. The residue, by extraction with ether, yielded a comparatively small amount of a viscid oil. After evaporation to dryness, the residue was heated with water at 400° for three hours. The gases formed included carbon dioxide and the vapour of a substance, most probably furan. The solid products were light coloured and slightly tarry. By steam distillation an oil of basic odour was obtained. The volatile acids included the lower fatty acids and benzoic acid. *iso*Phthalic acid and terephthalic acid were also obtained.

G. W. R.

Thermal Decomposition of Tetramethylammonium Fluoride. F. GONZÁLEZ NÚÑEZ (*Anal. Fis. Quim.*, 1922, 20, 539—549).—Tetramethylammonium fluoride is obtained in 89% yield by exact neutralisation of the hydroxide with hydrofluoric acid. When decomposed by heating in the presence of water catalysed by metals (silver, platinum, or copper) the products are nitrous oxide, methyl fluoride, trimethylamine, and methane.

G. W. R.

Mercuric Compounds with Hexamethylenetetramine. R. DOURIS and G. BEYTOUT (*Compt. rend.*, 1923, 176, 107—109).—When mercuric sulphate is dissolved in water to which is added drop by drop just sufficient sulphuric acid to prevent the formation of the basic sulphate and the solution is added to an equimolecular solution of hexamethylenetetramine the double *mercuric hexamethylenetetramine sulphate*,  $C_6H_{12}N_4SO_4Hg.H_2O$ , m. p. 177° (decomp.), is obtained. The double *cyanide* decomposing at 216° and the double *acetate* decomposing at 120° are similarly prepared. In these salts the corrosive action of the ordinary mercuric salt is considerably diminished and the therapeutic action increased.

W. G.

Hexamethylaminetetramine-betaine. F. BOEDECKER and J. SEPP (*Ber. Deut. pharm. Ges.*, 1922, 32, 339—344).—The reaction between hexamethylenetetramine and chloroacetic acid is so violent that profound decomposition ensues. The hydrochloride of the

betaine is formed in good yield, however, when these substances react in chloroform solution. The well-characterised compounds of hexamethylenetetramine-betaine with metallic halides are obtained in good yield by the action of hexamethylenetetramine on aqueous solutions of salts of chloroacetic acid. The hydrochloride of hexamethylenetetramine-betaine,  $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2H$ , obtained as indicated above in chloroform solution, forms large crystals which by treatment with moist silver oxide give the hydrated form of hexamethylenetetramine-betaine,  $OH \cdot C_6H_{12}N_4 \cdot CH_2 \cdot CO_2H$ , lustrous plates, easily soluble in water with neutral reaction and slightly sweet taste. By the action of hexamethylenetetramine on aqueous sodium chloroacetate, the sodium salt,  $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2Na \cdot H_2O$ , was obtained. Addition of aqueous cadmium chloride to its aqueous solution causes the double salt,  $(C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2)_2Cd \cdot CdCl_2 \cdot 4H_2O$ , to crystallise. This on treatment with hydrochloric acid gives the acid cadmium salt,  $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2H \cdot CdCl_2 \cdot H_2O$ . By the action of zinc chloride and mercuric chloride respectively on the solution of the sodium salt, double salts,  $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2Na \cdot ZnCl_2 \cdot H_2O$  and  $(C_6H_{12}N_4Cl \cdot CMe \cdot CO_2)_2Hg \cdot HgCl_2$ , were obtained. P. M.

**The Chlorination of Esters of Amino-acids.** WILHELM TRAUBE and HEINRICH GÖCKEL (*Ber.*, 1923, 56, [B], 384–391).—Ethylurethane can be smoothly converted by chlorine or hypochlorous acid in aqueous solution into *N*-chloroethylurethane,  $NHCl \cdot CO_2Et$ . Under similar conditions, the conversion of the esters of amino-acids into the corresponding monochlorinated derivatives does not appear to be possible, the dichloro-compounds being almost invariably produced.

Ethylurethane dissolved in water is converted by gaseous chlorine at the atmospheric temperature into *N*-chloroethylurethane, b. p. 101–102°/30 mm., the yield being 80% of that theoretically possible. It solidifies at 0°. The potassium salt,  $C_3H_5O_2NClK \cdot 2H_2O$ , lustrous prisms which explode at 300°, the hygroscopic sodium salt, and the silver salt, a colourless powder, are described. *N*-Chloro-*N*-methylurethane,  $NMeCl \cdot CO_2Et$ , a colourless liquid, b. p. 57°/30 mm., is prepared by the chlorination of *N*-methylurethane or by the action of methyl sulphate and potassium hydroxide on chloroethylurethane. The latter is transformed by potassium hydroxide and benzoyl chloride into *N*-chloro-*N*-benzoylurethane, a pale yellow liquid which was not prepared in the homogeneous condition; its formation is established by the reduction of the product of the reaction to *N*-benzoylurethane, m. p. 110°. The action of ethyl chloroformate on chloroethylurethane in aqueous alkaline solution leads to the production of a mixture of *N*-dichloroethylurethane, b. p. 73°/20 mm., and ethyl imino-dicarboxylate, m. p. 50°; the primarily formed ethyl chloroimino-dicarboxylate appears to react with a portion of the chloroethylurethane liberated by hydrolysis of the potassium salt in accordance with the scheme:  $NCl(CO_2Et)_2 + Cl \cdot NH \cdot CO_2Et \rightarrow NH(CO_2Et)_2 + NCl_2 \cdot CO_2Et$ .

The action of chlorine on an aqueous solution of ethyl amino-

acetate leads to the formation of *ethyl dichloroaminoacetate*,  $\text{NCl}_2\text{CH}_2\text{CO}_2\text{Et}$ , a yellow liquid. *Ethyl dibromoaminoacetate* is prepared from ethyl aminoacetate and sodium hypobromite; both dihalogenated compounds are unstable. *Ethyl  $\alpha$ -dichloroamino-propionate*,  $\text{NCl}_2\text{CHMeCO}_2\text{Et}$ , is an extremely unstable, pale yellow liquid. H. W.

**Synthesis of  $\gamma$ -Amino- $\beta$ -hydroxybutyric Acid.** MASAJI TOMITA (*Z. physiol. Chem.*, 1923, 124, 253—258).— $\gamma$ -Phthalimido- $\beta$ -hydroxybutyronitrile, m. p. 132°, is prepared by the action of potassium cyanide on  $\alpha$ -chloro- $\gamma$ -phthalimido- $\beta$ -hydroxypropane. When hydrolysed with concentrated sulphuric acid at water-bath temperature, it yields  $\gamma$ -amino- $\beta$ -hydroxybutyric acid, m. p. 214°, which gives a marked biuret reaction, and forms a crystalline copper salt. When heated just above its melting point, it loses water to form 4-hydroxy-2-pyrrolidone, m. p. 118°, and on exhaustive methylation the betaine is formed, isolated as its chloroaurate,  $\text{C}_4\text{H}_{11}\text{O}_3\text{N}_2\text{HAuCl}_4$ , citron-yellow needles, m. p. 180—182°. It has been suggested that carnitine may be the betaine of  $\gamma$ -amino- $\beta$ -hydroxybutyric acid, but carnitine chloroaurate melts about 30° lower than that of the betaine described above. There remains, however, the possibility that carnitine may be the optically active form. W. O. K.

**A Polymeride of Hydrocyanic Acid.** CH. BEDEL (*Compt. rend.*, 1923, 176, 168—171).—When azulmin, resulting from the polymerisation of hydrocyanic acid, is extracted with ether, a yellowish-brown, crystalline substance is obtained. If this material is crystallised from aqueous solution after decolorising it with animal charcoal and the resulting mother-liquors are concentrated in the presence of charcoal, a colourless, crystalline substance is obtained. It has m. p. 179° (decomp.), and molecular-weight determinations show it to be a tetrameride of hydrogen cyanide. When decomposed by dilute mineral acids, it gives for each molecule one molecule of hydrogen cyanide. When decomposed by barium hydroxide, it gives glycine, ammonia, and a small amount of barium carbonate, but principally barium oxalate. With alcoholic potassium hydroxide and chloroform, it gives the odour of carbonylamine. From its behaviour the author considers it to be a hydrocyanide of aminopropanedinitrile (cf. Wippermann *Ber.*, 1874, 7, 767). W. G.

**The Nitriles of Fluoro- and Difluoro-acetic Acids.** FRED SWARTS (*Bull. Soc. chim. Belg.*, 1922, 31, 364—365).—These substances were prepared by distillation of the corresponding amide with phosphoric oxide. *Fluoroacetonitrile* is a colourless liquid of penetrating odour, b. p. 81.8—82°,  $d_4^{20}$  1.0730. It is slightly soluble in water and reacts rapidly with potassium hydroxide. *Difluoroacetonitrile*, b. p. 22.8—23.4°, is a colourless, mobile liquid  $d_4^{20}$  1.1130, very sparingly soluble in water and reacting vigorously with potassium hydroxide. A specimen kept for several years did not undergo polymerisation. H. J. E.

**The Action of Organomagnesium Compounds on Nitriles.**  
***n*-Butyronitrile.** FRANTZ BAERTS (*Bull. Soc. chim. Belg.*, 1922, 31, 421—426).—The results obtained with *n*-butyronitrile are exactly parallel to those previously obtained by the author with propionitrile (A., 1922, i, 817). The chief product of *n*-butyronitrile and magnesium ethyl bromide was ethyl propyl ketone (about 40%). Diethylpropylcarbinol was also formed together with termolecular cyanopropane,  $(\text{PrCN})_3$ , and a substance not previously isolated which proved to be  $\alpha$ -butyrylbutyronitrile, a liquid, b. p.  $216^\circ$ , semicarbazone, m. p.  $88$ — $90^\circ$ . P. M.

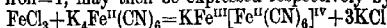
**Constitution of Allyl Cyanide.** P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1920, 479—486).—Pyridine and  $\gamma$ -chlorobutyronitrile when heated together give allyl cyanide, b. p.  $114$ — $116^\circ/757$  mm.,  $d_4^{20}$  0.8318,  $n_D^{20}$  1.41438. The product is not accompanied by the nitrile of cyclopropanecarboxylic acid, which, however, is formed by the action of dry potassium hydroxide on the above chloro-compound, whilst the latter with sodium ethoxide affords a mixture of the cyclic nitrile and  $\gamma$ -ethoxybutyronitrile.

By the removal of the elements of water from  $\alpha$ -hydroxybutyronitrile, a product (b. p.  $115$ — $116^\circ/763$  mm.,  $n_D^{20}$  1.41692) is obtained, which, from its convertibility into two known dibromo-amides is thought to be a mixture of crotononitrile and isocrotononitrile. Potassium cyanide and allyl bromide interact to give the same mixture. E. E. T.

**Prussian Blue and Turnbull's Blue.** V. ERICH MÜLLER [with HANS LAUTERBACH] (*J. pr. Chem.*, 1922, [ii], 104, 241—258).—The insoluble Prussian blue, precipitated by adding potassium ferrocyanide solution to ferric chloride solution in the proportion non-ionisable iron : ionisable iron = 0.75, consists of ferric ferrocyanide, which is converted by further addition of potassium ferrocyanide into potassium ferric ferrocyanide. Equimolecular proportions of potassium ferrocyanide and ferric chloride do not, however, give pure potassium ferric ferrocyanide, because the reaction  $\text{Fe}_4^{III}[\text{Fe}^{II}(\text{CN})_6]_{13}^{IV} + \text{K}_4\text{Fe}^{II}(\text{CN})_6 \rightleftharpoons 4\text{KFe}^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$  is reversible, and the further change  $\text{KFe}^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV} + \text{K}_4\text{Fe}^{II}(\text{CN})_6 = \text{K}_5\text{Fe}^{III}(\text{CN})_6 + \text{K}_3\text{Fe}^{II}[\text{Fe}^{II}(\text{CN})_6]^{IV}$  occurs, so that the main product,  $\text{KFe}^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$ , contains traces of potassium ferrous ferrocyanide and ferric ferrocyanide in solid solution. The insoluble Turnbull's blue, formed by adding potassium ferri-cyanide to ferrous chloride solution in the proportion non-ionisable iron : ionisable iron = 0.75, is  $\text{KFe}^{II}\text{Fe}_3^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$ , which with further amounts of potassium ferricyanide passes into potassium ferric ferrocyanide :

$\text{KFe}^{II}\text{Fe}_3^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV} + \text{K}_3[\text{Fe}^{III}(\text{CN})_6]^{III} = 4\text{KFe}^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$ . Again, the proportion non-ionisable iron : ionisable iron = 1.0 gives a solid solution, consisting mainly of  $\text{KFe}^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$ , with traces of  $\text{KFe}^{II}\text{Fe}_3^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$ , and also of  $\text{Fe}_4^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV}$ , formed according to the equation  $\text{KFe}^{II}\text{Fe}_3^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV} + \text{K}_3\text{Fe}^{III}(\text{CN})_6 = \text{Fe}_4^{III}[\text{Fe}^{II}(\text{CN})_6]^{IV} + \text{K}_4\text{Fe}^{II}(\text{CN})_6$ . The formation of

Prussian blue and of Turnbull's blue, when non-ionisable iron : ionisable iron = 1, may then be expressed respectively by :



and



Suppose for the formation of Turnbull's blue a ferricyanide solution is used containing 1 mol. KCl per mol.  $\text{FeCl}_2$ , so that there can be written  $\text{FeCl}_2 + \text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl} = \text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{\text{IV}} + 3\text{KCl}$ , then both reactions become fully identical if the primary change is :  $\text{FeCl}_2 + \text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl} = \text{FeCl}_3 + \text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ . Equimolecular solutions of (a)  $\text{FeCl}_3$  and  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ , (b)  $\text{FeCl}_2$  and  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl}$  therefore give the same end-product, the Prussian blue and Turnbull's blue formed under these conditions being identical.

These views, which agree with results already obtained analytically (cf. A., 1909, i, 142, 705, 706; 1911, i, 844; 1914, i, 504, 1058), have now been fully confirmed by following the various reactions potentiometrically; the potential of a platinum electrode immersed in one reagent is compared with that of a normal electrode ( $\text{Hg}, \text{Hg}_2\text{Cl}_2, \text{N} - \text{KCl}$ ) after each addition of the second reagent. The results are shown graphically, the volume of the added constituent being plotted against the compensating ohmic resistance. The formation of solid solutions is deduced from the gradual slope of the relevant curves, whilst the intersection at the point "non-ionisable iron : ionisable iron = 1" of all four curves, corresponding with the pairs of reagents (1)  $\text{FeCl}_3$  and  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ , (2)  $\text{FeCl}_2$  and  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl}$ , is considered proof of the identity of the Prussian blue and the Turnbull's blue formed under these conditions.

W. S. N.

**Derivatives of Semioxamizide. I. Ketonic Semioxamazones.** FORSYTH JAMES WILSON and ERIC CHARLES PICKERING (T., 1923, 123, 394—397).

**Oxidation of Cadets' Oil. Preparation of Cacodylic Acid.** HENRI GUINOT (*J. Pharm. Chim.*, 1923, [vii], 27, 55—64).—The mixture of cacodyl and cacodyl oxide obtained by the dry distillation of potassium acetate and arsenious oxide is oxidised quantitatively to cacodylic acid by aqueous hypochlorite solutions, and the same reaction may be utilised for its estimation, the excess of hypochlorite added being determined by the addition of potassium iodide and titration of the liberated iodine with thiosulphate. For the preparation of cacodylic acid, the oil is agitated with the requisite amount of sodium hypochlorite solution in presence of hydrochloric acid, the completion of the oxidation being indicated by the disappearance of the odour of cacodyl or by the use of potassium iodide-starch paper. The acid solution thus obtained is neutralised with sodium hydroxide, using Congo-red as indicator, and is then evaporated to a small bulk, and the sodium chloride which separates is removed. The syrup is finally evaporated to dryness, and extracted with 96% alcohol. The alcoholic extract on cooling deposits pure cacodylic acid in 70% yield, and another 20% may

be obtained from the mother-liquors. Alternatively, cacodylic acid may be obtained in 80% yield by direct oxidation by means of oxygen of a solution of the oil in dry acetone to which slightly more than the amount of water theoretically required by the following equations is gradually added as the absorption of oxygen proceeds:  $(\text{AsMe}_2)_2\text{O} + \text{H}_2\text{O} + \text{O}_2 = 2\text{AsMe}_2\text{O} \cdot \text{OH}$  and  $2(\text{AsMe}_2)_2 + 2\text{H}_2\text{O} + 3\text{O}_2 = 4\text{AsMe}_2\text{O} \cdot \text{OH}$ . The absorption of oxygen is very rapid and is with advantage moderated somewhat, otherwise a certain amount of arsenious acid will be formed. The cacodylic acid formed crystallises from the solution in an almost pure condition. The anodic oxidation of a solution of the oil in 20% sulphuric acid also gives a 70–80% yield of cacodylic acid, but this method does not present any practical advantage.

G. F. M.

**Permanence of the Grignard Reagent.** HENRY GILMAN and CHARLES H. MEYERS (*J. Ind. Eng. Chem.*, 1923, 15, 61).—Observations extending over more than six months showed that the numerous Grignard reagents examined underwent no appreciable deterioration or decomposition during this period, when kept in ethereal solution (in some cases highly concentrated) and adequately protected from the moisture, carbon dioxide, and oxygen of the atmosphere by storage in glass-stoppered containers.

G. F. M.

**The Optimum Condition for the Preparation of Magnesium Ethyl Iodide.** HENRY GILMAN and CHARLES H. MEYERS (*J. Amer. Chem. Soc.*, 1923, 45, 159–165).—Using the methods of analysis previously described (*ibid.*, 150) and a special reaction flask by means of which it was possible to withdraw aliquot portions for analysis, a study was made of the factors which influence the yield of magnesium ethyl iodide and, therefore, to some extent the yield of other Grignard reagents. The results indicate that there is a steady increase in the percentage of Grignard reagent formed when the rate of addition of ethyl iodide is progressively decreased, but that no advantage is gained by extending the time for the addition of 9.5 g. of ethyl iodide beyond forty-five minutes. Stirring during the addition of the ethyl iodide and for fifteen minutes after the addition is completed is desirable, and then it is not necessary to warm the mixture under a reflux condenser. Any large excess of magnesium does not affect the yield. When no precautions are taken to exclude the moisture and carbon dioxide of the air, the yield is lowered. Under a standard set of conditions the finer the grade of magnesium turnings used, the higher is the yield.

W. G.

**Reducing Action of Grignard Reagents.** B. A. BUYLLA and E. OLAY (*Anal. Fis. Quim.*, 1922, 20, 599–600).—Metallic alkylloxides react with Grignard reagents, giving hydrocarbons. For example, magnesium ethyl iodide and sodium methoxide in the presence of anhydrous xylene with ethyl ether or dimethyl-aniline as catalyst react as follows:  $\text{MgEtI} + \text{MeONa} = \text{C}_2\text{H}_4 +$

$\text{CH}_4 + \text{MgO} + \text{NaI}$ . Ethyl magnesium iodide and sodium amyl-oxide give ethylene and an unidentified liquid hydrocarbon.

G. W. R.

**The Preparation of Methylmercuric Acetate and the Isolation of Methylmercuric Hydroxide.** M. CANNON SNEED and J. LEWIS MAYNARD (*J. Amer. Chem. Soc.*, 1922, **44**, 2942—2947).—The substance described by Otto (*Annalen*, 1870, **154**, 199) as methylmercuric acetate, m. p. 142—143°, could not have been pure. The authors have obtained pure methylmercuric acetate by four different methods, namely, (1) the action of mercuric acetate on mercurydimethyl in methyl alcohol, (2) the neutralisation of methylmercuric hydroxide with glacial acetic acid, (3) the action of methylmercuric hydroxide on ethyl acetate, (4) the interaction of silver acetate and methylmercuric iodide. So prepared, it has, in all cases, m. p. 128°, and is very soluble in water, acetic acid, and ethyl alcohol. It is also one of the products of the thermal decomposition of mercurous acetate in an atmosphere of nitrogen.

*Methylmercuric hydroxide*, m. p. 95°, is readily obtained by the action of moist silver oxide on methylmercuric iodide in methyl alcohol. It is a very weak base, being alkaline to litmus but acid to phenolphthalein in aqueous solution. It is a strong vesicant even in dilute solutions.

W. G.

**Ethyl Ether- and Ethanol-mercuri-salts.** K. A. HOFMANN and KURT LESCHEWSKI (*Ber.*, 1923, **56**, [B], 123—129).—Hofmann and Sand have assigned the constitutions  $\text{X} \cdot \text{Hg} \cdot \text{C}_2\text{H}_5 \cdot \text{OH}$  and  $\text{X} \cdot \text{Hg} \cdot \text{C}_2\text{H}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_5 \cdot \text{HgX}$  to the products obtained by the action of ethylene on mercury salts, whereas according to Manchot (*A.*, 1920, i, 519, 720) they are to be regarded as additive products,  $\text{C}_2\text{H}_5 \cdot \text{HgX} \cdot \text{OH}$ , analogous to the compound obtained from cuprous chloride and carbon monoxide. The readiness with which they evolve ethylene appears to support Manchot's conception, but, on the other hand, the same tendency is observed with undoubtedly atomic compounds, such as ethylene dibromide, which yields ethylene when treated with magnesium or organomagnesium compounds and magnesium ethyl bromide, which evolves the gas when treated with manganese chloride. The mercuri-salts are somewhat sharply differentiated from Manchot's compounds of cuprous chloride with ethylene or carbon monoxide by their much greater stability towards non-acidic reagents and heat. The strongest argument in favour of the conception of the existence of an alcoholic group in ethanolmercuri-compounds lies in the observation that they evolve alcohol and aldehyde when boiled with potassium hydroxide solution and leave a residue of metallic mercury and mercuride,  $\text{C}_2\text{H}_5\text{O}_2\text{Hg}_2$ . The change proceeds slowly when potassium hydroxide alone is used, but can be greatly accelerated by the addition of potassium iodide; under the latter conditions, 50% of the organic portion of ethanolmercuri-chloride is obtained as alcohol and aldehyde, the production of the latter being attributable to the oxidising action of mercury oxide in the

strongly alkaline medium. The action is very difficult to explain Manchot's mode of formulation is adopted, since the persistence of portions of the mercuri-compound until the conclusion of the change shows that hydratisation of ethylene does not occur previously to its evolution and an alkaline suspension of mercury oxide is found to be without appreciable action on pre-formed ethylene.

H. W.

**Primary Tar.** I. FRANZ SCHÜTZ (*Ber.*, 1923, 56, [B], 162—169).—An examination of the tar formed by the carbonisation of coal obtained from the neighbourhood of Dortmund in rotary furnaces at 500—600°. The coal yields about 23% of volatile products (about 7% tar, 6% aqueous distillate, and 10% gas) and about 77% of semi-coke. It is found that the most volatile portions of the neutral oils contain only very small quantities of paraffins and larger amounts of unsaturated hydrocarbons. They consist mainly of aromatic and hydroaromatic hydrocarbons. The presence of benzene, toluene, and xylene is established, and that of their higher homologues is shown to be probable. The presence of considerable amounts of hydroaromatic hydrocarbons may be regarded as extremely probable. The absence of naphthalene is confirmed. Ketones, particularly acetone, are present. Phenol occurs in considerable quantity, its amount being very much greater than in coke-oven tar. Traces of acetaldehyde and acetonitrile are observed. Toly! mercaptans are present in very small amount together with a sulphide, b. p. 150—160°, which appears to belong to the aliphatic series.

H. W.

**Preparation of Petroleum from Rosin.** SEIJI KWAI (*J. Chem. Ind. Japan*, 1922, 25, 1421—1424).—On distilling a mixture of rosin (acid value 162.1 and saponification value 178.3) and dried Japanese acid earth (ratio 1 : 0.5—1 : 2) at 160° to 350° under ordinary pressure, an oily distillate, *d* 0.88, was produced; the yield being about 60% of the rosin used. This had an odour and a marked fluorescence similar to that of natural petroleum and is approximately composed of naphthenes, about 50%, aromatic hydrocarbons 40%, and unsaturated hydrocarbons (probably terpenes) 10%.

K. K.

**Lely's Benzene Formula.** S. C. J. OLIVIER (*Chem. Weekblad*, 1923, 20, 27).—A criticism of the triangular formula (this vol., i, 99). The synchronous rotation of the hydrogen atoms or substituents attached to the secondary carbon atoms is a dangerous conception; applied to the four dissimilar atoms or groups attached to an asymmetric carbon atom, it would invalidate the possibility of optical isomerism. Further, the existence of meta- and ortho-substituted benzenes is only possible if the phase of the synchronous rotation is unalterable in molecular collisions, reactions, etc. The facts with regard to substitution generally are only explained by Lely's arguments which could equally easily be employed to lead to exactly opposite conclusions.

S. I. L.

**The Essentials of a Benzene Formula.** H. J. PRINS (*Chem Weekblad*, 1923, 20, 28; see preceding abstract).—Lely's formula fails entirely to explain the characteristic properties of the aromatics as contrasted with the aliphatic compounds; if benzene contained  $-\text{CH}_2-$  groups, all the mono-substituted benzenes should act as if the substituent were united to a carbon atom still united to hydrogen e.g., phenol like a secondary alcohol. Quinol would have the group  $\text{C} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$  and ring formation as in phthalic anhydride should occur equally readily with para-substituted derivatives, as terephthalic acid.

S. I. L.

**The Structural Formula for Benzene.** H. A. J. SCHOUTISSEN (*Chem. Weekblad*, 1923, 20, 29; see preceding abstracts).—The four valencies of the primary carbon atoms in Lely's formula lie in one plane, and in an angle of  $130^\circ 32'$ , making with each other angles of  $35^\circ 16'$  and  $60^\circ$ . The valencies of the three secondary carbon atoms lie along the edges of a tetrahedron. Such a distribution in a stable system like benzene is unthinkable.

A space-model of benzene based on the Lewis-Langmuir theory is suggested, which has the necessary symmetry and valency-distribution. In one phase it coincides with that of Pauly (*A.*, 1919, i, 120), whilst by a rotation of each of the carbon atoms through  $90^\circ$  or  $270^\circ$  the configuration of Armstrong, Baeyer, and Claus is obtained.

S. I. L.

**Cymene as a By-product of the Hydrolysis of Wood.** EMIL HEUSER, L. ZEH, and B. ASCHAN (*Z. angew. Chem.*, 1923, 36, 37–38).—*p*-Cymene occurs in appreciable quantities amongst the volatile products of the hydrolysis of wood with dilute mineral acids under pressure, and originates probably from the action of the acid on the  $\alpha$ -pinene derived from the resins of the wood. It was isolated from the light oil which collects on the surface of the distillate. This was treated with sodium hydrogen sulphite to remove furfuraldehyde, and with 40% potassium hydroxide to remove volatile acids, and then fractionally distilled. The fraction boiling between  $174^\circ$  and  $179^\circ$  consisted largely of *p*-cymene which was identified by conversion into barium *p*-cymenesulphonate. The total content of *p*-cymene in the light oil was estimated at 4–5%.

G. F. M.

**1-Methyl-3-tert.-amylbenzene.** G. CHARRIER [with M. GALLOTTI and E. ZAPPELLI] (*Gazzetta*, 1922, 52, ii, 317–323).—By the action of *tert*-amyl chloride on toluene in presence of aluminium chloride, the author has obtained the compound prepared by Essner and Gossin (*A.*, 1885, 517) by treating toluene in presence of aluminium chloride with either active or inactive amyl chloride or amylene. The conclusion drawn by these authors that this compound is 1-methyl-3-*tert*-amylbenzene is confirmed, its description in Beilstein (edition III, ii, 36) as *m*-isoamyltoluene being inaccurate.

1-Methyl-3-*tert*-amylbenzene is a colourless, mobile, refractive liquid with an odour of pine resin,  $d_4^{20}$  0.8930,  $d_4^{25}$  0.8673,  $d_4^{30}$  0.8082.

When oxidised by either permanganate or dilute nitric acid, it yields isophthalic acid. The action of fuming nitric acid at  $-10^{\circ}$  gives two isomeric *mononitro*-derivatives, which are uncrystallisable, pale yellow liquids with a pungent odour of musk: (1) b. p.  $160-161^{\circ}/25$  mm.,  $d_4^{20}$  1.0675, and (2) b. p.  $165-169^{\circ}/23$  mm.,  $d_4^{20}$  1.0825; the nitro-groups probably occupy the 2-, 4-, or 6-positions.

The action of chlorine on the hydrocarbon in presence of iodine yields two *monochloro*-derivatives, probably the 4- and 6-compounds: (1) a mobile, highly refractive liquid with a delicate odour of aniseed, b. p.  $242-243^{\circ}/750.25$  mm.,  $d_4^{20}$  0.9769, and (2) a highly refractive liquid with a similar odour to the previous compound, b. p.  $247-248^{\circ}/750.25$  mm.,  $d_4^{20}$  1.0111; neither isomeride solidifies at  $-25^{\circ}$ .

The action of bromine on the hydrocarbon in the dark at  $0^{\circ}$  gives 4-(or 6) *bromo-1-methyl-3-tert.-amylbenzene*, which is a highly refractive liquid with a pleasing ethereal odour, b. p.  $262-264^{\circ}/752.38$  mm.,  $d_4^{20}$  1.2143, and remains liquid at  $-25^{\circ}$ . T. H. P.

**The Influence of some Substituents in the Benzene Ring on the Mobility of the Chlorine in the Side-chain in its Relation to the Problem of Substitution in the Benzene Ring. II.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1922, 41, 646-651; cf. A., 1922, i, 646).—A development of the work described in the previous paper. The influence of the position of the substituent is less pronounced the greater the retarding influence of that substituent on mobility. A table is given showing the values of the reaction constants calculated from the rate of saponification of various compounds, that for benzyl chloride itself being taken as unity. From this it is seen that at a higher temperature the reaction velocities generally tend to become of identical value, the smaller increasing with temperature, the greater remaining approximately constant. The retarding influence of the negative substituents is thus less pronounced at a higher temperature. The list of substituents in their order of influence as previously given (*loc. cit.*) is now amplified by addition of bromine and is  $p\text{-Me} > o\text{-Me} > m\text{-Me} > \text{H} > p\text{-Cl} > p\text{-Br} > o\text{-Cl} > o\text{-Br} > m\text{-Cl} > m\text{-Br} > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-NO}_2$ . H. J. E.

**Some Constants of Phenylchloroform [Tri-*o*-chlorotoluene].**

FRED. SWARTS (*Bull. Soc. chim. Belg.*, 1922, 31, 375-377).—A redetermination of some of the physical constants of tri-*o*-chlorotoluene gave the following values: m. p.  $-4.75^{\circ}$ ; b. p.  $110.7^{\circ}/23$  mm.;  $220.7^{\circ}/761$  mm.;  $d_4^{20}$  1.3775. The cryoscopic constant has the notably high value 93.1. Moist air in contact with the substance causes rapid and considerable lowering of the freezing point, previous values for which are  $-22.5^{\circ}$  (Haas, A., 1893, ii, 357),  $-17^{\circ}$  (Altschul, A., 1895, ii, 206), and  $-8.1^{\circ}$  (Timmermans, A., 1914, ii, 168). H. J. E.

**Aromatic Sulphinic Acids.** E. KNOEVENAGEL and A. RÖMER (*Ber.*, 1923, 56, [B], 215-217).—Sodium benzenesulphinate in the presence of ether is converted by one or less molecular proportion of phosphorus trichloride into *phenyl benzenethiosulphonate*,

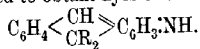
$\text{Ph}\cdot\text{SO}_2\cdot\text{SPh}$ , m. p.  $45^\circ$ , which is reduced by an excess of the tri-chloride to diphenyl disulphide, m. p.  $60^\circ$ . Under similar conditions, thionyl chloride yields benzenesulphonyl chloride, phenyl benzenethiosulphonate, and some nitrogen sulphide. Sulphuryl chloride gives benzenesulphonyl chloride.

Salts of the type  $\text{CHR}\cdot\text{NHR}'\cdot\text{SO}_2\text{Ph}$  are obtained by the action of molar amounts of benzenesulphonic acid and anils in the presence of ether at the atmospheric temperature. These are decomposed by solution in alcohol and subsequent addition of ether in accordance with the equations:  $\text{CHR}\cdot\text{NHR}'\cdot\text{SO}_2\text{Ph} + \text{H}_2\text{O} = \text{R}\cdot\text{CHO} + \text{R}'\cdot\text{NH}_2 + \text{Ph}\cdot\text{SO}_2\text{H}$ ;  $3\text{Ph}\cdot\text{SO}_2\text{H} = \text{Ph}\cdot\text{SO}_3\text{H} + \text{Ph}\cdot\text{SO}_2\cdot\text{S}\cdot\text{Ph} + \text{H}_2\text{O}$ ;

$\text{Ph}\cdot\text{SO}_2\text{H} + \text{Ph}\cdot\text{NH}_2 = \text{Ph}\cdot\text{NH}_2 \begin{smallmatrix} \text{H} \\ \text{SO}_2\text{Ph} \end{smallmatrix}$ . The salts derived from the following anils have the melting points placed in brackets: benzylideneaniline ( $82^\circ$ ); benzoinanil ( $158-160^\circ$ ); acetophenoneanil ( $136^\circ$ ); dypnoneanil ( $130^\circ$ ). Acetoneanil and *N-isopropenyl-N-methylaniline* appear to react in a more complicated manner.

Ferrous and ferric benzene sulphinates are almost insoluble in water; the nickel, cobalt, copper, and cadmium salts dissolve to the extent of 10–15% in boiling water, the manganese salt to 20%, and the lead and silver salts to 40%. Aluminium and chromium salts do not give a precipitate with benzenesulphonic acid. The manganese, copper, and lead salts are soluble in dilute acetic acid; the cadmium salt dissolves in glacial acetic acid, whereas the nickel, cobalt, and iron salts require dilute mineral acids to bring them into solution. H. W.

**Certain Derivatives of Anthracene.** F. KEHRMANN, RAOUL MONNIER, and MARIE RAMM (*Ber.*, 1923, 56, [B], 169–174).—Attempts are described to obtain dyes of the type



The nitration of 9:10:10-triphenyl-9:10-dihydroanthran-9-ol (Haller and Guyot, A., 1904, i, 660) could not be satisfactorily accomplished.

9-Phenyl-10:10-diethyl-9:10-dihydroanthran-9-ol, colourless needles, m. p.  $111-112^\circ$ , is prepared by the action of magnesium phenyl bromide on 10:10-diethyl-9-anthrone; it forms coloured carbonium salts with sulphuric, perchloric, and nitric acids. When dissolved in concentrated sulphuric acid it is converted by alcohol into 10-phenyl-9:9-diethyl-9:10-dihydroanthracene, colourless needles, m. p.  $135-136^\circ$ . 9:9-Diethyl-9:10-dihydroanthracene, slender, colourless needles, m. p.  $210^\circ$ , is obtained by the reduction of diethylanthrone with zinc dust and acetic acid.

9:10-Diphenyl-9:10-dihydroanthra-9:10-diol (Haller and Guyot, *loc. cit.*) gives an intense indigo-blue solution in concentrated sulphuric acid; it appears to be transformed thereby into anthraquinone, 9:10-diphenylanthracene, and an intensely reddish-yellow substance which has not been completely investigated. The nitration and reduction of the products will be described subsequently. H. W.

**Preparation of Cyclic Amines.** A. MAILHE (*Bull. Soc. chim.*, 1923, [iv], **33**, 83—86).—The direct hydrogenation of the hydrazones or ketazines of cyclic ketones over a nickel catalyst at 180° leads, as in the case of similar open-chain compounds, to the formation of primary amines accompanied by a small proportion of the corresponding secondary amines. Thus the hydrazone of 1:3-dimethyl-4-cyclohexanone is converted into 1:3-dimethyl-4-cyclohexylamine, a colourless liquid, b. p. 169—171°,  $d^{20}_4$  0.8810, which rapidly absorbs carbon dioxide from the air and gives a hydrochloride, m. p. 278°, and a phenylcarbamide, m. p. 174°. Similarly, carvylamine is obtained together with a small quantity of dicarvylamine by the hydrogenation of carvone ketazine. Carvylamine boils at 205—210°, and forms a hydrochloride, m. p. 198°. Menthylamine obtained by the hydrogenation of menthonehydrazone, a colourless liquid, b. p. 243°, over nickel at 200°, is a strong base, b. p. 212°, giving a hydrochloride, m. p. 274°. Dimethylamine produced at the same time boils at 305—310°, and gives a hydrochloride, m. p. 207°. G. F. M.

**Formation of Phenylcarbylamine and Nitrobenzene in Aqueous Aniline Solutions.** HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. Deut. pharm. Ges.*, 1922, **32**, 232—236).—The formation of products with an odour of carbylamine when aniline and water are exposed for several months to sunlight does not take place if the aniline is pure, the products in this case being of a tarry nature and dissolving in concentrated sulphuric acid with a Bordeaux-red colour. Mono-methyl- and ethyl-anilines and toluidine behave in the same way as aniline. On the other hand, minute traces of nitrobenzene are formed even with pure aniline under the above conditions. P. M.

**Action of Alcohols on Anilides.** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1923, [iv], **33**, 81—83).—Although the hydrogen atom of the  $\text{NH}=\text{N}$  group of secondary arylamines is readily replaced by an alkyl group by the action of aliphatic alcohols in presence of dehydrating catalysts such as thoria or alumina, the aromatic amides cannot be similarly alkylated, as the water produced in the reaction causes the hydrolysis of the amides. So, for example, the catalysis of a mixture of acetanilide and methyl alcohol vapours over alumina at 370—380° results, not in the formation of methyl-acetanilide, but of a mixture of aniline, methylaniline, and dimethylaniline and acetic acid, together with small quantities of dimethyl ether. Other anilides and toluidides behave in a similar manner either with methyl or ethyl alcohol. With propyl alcohol, propylene and water are formed, and the anilide is hydrolysed; but no propylanilines are produced. G. F. M.

**The Action of Sodammonium on Aniline and its Homologues.** M. PRION (*Compt. rend.*, 1922, **175**, 1213—1216).—The action of sodammonium on cyclic amines in which the nitrogen is directly linked to the benzene ring affords a ready method of preparing the sodium derivatives of these amines. Only

monosodium derivatives were obtained; these are formed as readily with primary as with secondary amines. No reaction occurs with benzylamine. Monosodioaniline,  $\text{NPhNa}$ , is a pale yellow, transparent solid decomposed by water with formation of aniline and sodium hydroxide and reacting with alkyl halides yielding substituted anilines (cf. Titherley, T., 1897, 71, 464). *Sodio-ethylaniline*,  $\text{NPhEtNa}$ , is a pale yellow solid; *monosodio-toluidine*,  $\text{C}_6\text{H}_4\text{MeNHNa}$ , a pale yellow solid; *sodiodiphenylamine*,  $\text{NPh}_2\text{Na}$ , a white solid; they all show properties similar to those of monosodioaniline. The method of preparation consists in mixing the amine with sodammonium and an excess of liquid ammonia and allowing the mixture to remain in contact under pressure at the ordinary temperature for some days. Attempts to prepare disodium derivatives were unsuccessful.

H. J. E.

**Reaction between Aniline and Chloroacetic Acid. I.** RYUZABURO NODZU and SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1922, 6, 73—76).—Among the products of interaction of aniline (1.04 mol.) and chloroacetic acid (1 mol.) in a closed vessel at  $100^\circ$  were isolated and identified chloroacetanilide, diketodiphenylpiperazine, phenyliminodiacetic acid and its mono-anilide, and phenylglycine. The mono-anilide is probably formed by the interaction of phenylglycine and chloroacetanilide.

E. H. E.

**Optically Active Dyes. I.** A. W. INGERSOLL and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 2930—2937).—In order to investigate the question as to whether the absorption of dyes by animal or vegetable fibres is a physical or chemical phenomenon the authors propose to prepare a number of optically active dyes and to examine the rate of absorption of the optical isomerides. With this purpose in view, they have prepared two such pairs of dyes. *d*- and *l*-aminoPhenylacetic acid have been condensed with *p*-nitrobenzoyl chloride and the products reduced to the corresponding amino-compounds, which were then diazotised and the diazo-compounds coupled with  $\beta$ -naphthol and dimethylaniline, respectively. Preliminary dyeing experiments have been carried out, and although the *d*- and *l*- $\beta$ -naphthol dyes were absorbed in the same relative amounts over short as well as long periods, the experiments with the two dimethylaniline dyes indicated that one is absorbed more rapidly than the other. The following new compounds are described: *r-p-Nitrobenzamidophenylacetic acid*, m. p.  $184^\circ$  (corr.), its *ethyl ester*, m. p.  $140^\circ$  (corr.). *r-p-Aminobenzamidophenylacetic acid*, m. p.  $152^\circ$  (corr.), and its *hydrochloride*, m. p.  $213^\circ$  (decomp.). *l-p-Nitrobenzamidophenylacetic acid*, m. p.  $163^\circ$  (corr.),  $[\alpha]_D^{20} - 86.56^\circ$ , its *ethyl ester*, m. p.  $155^\circ$  (corr.),  $[\alpha]_D^{20} - 67.7^\circ$ . *l-p-Aminobenzamidophenylacetic acid*, m. p.  $168-169^\circ$  (corr.),  $[\alpha]_D^{20} - 93.75^\circ$ , and its *hydrochloride*, m. p.  $220-222^\circ$  (decomp.). *d-p-Nitrobenzamidophenylacetic acid*, m. p.  $163^\circ$  (corr.),  $[\alpha]_D^{20} + 86.13^\circ$ , its *ethyl ester*, m. p.  $155^\circ$  (corr.),  $[\alpha]_D^{20} + 67.4^\circ$ . *d-p-Aminobenzamidophenylacetic acid*, m. p.  $168-169^\circ$  (corr.),  $[\alpha]_D^{20} + 93.63^\circ$ , and its *hydrochloride*, m. p.  $220^\circ$  (decomp.). The

$\alpha$ -aminobenzoyl acid when diazotised and the product coupled with  $\beta$ -naphthol gave a compound, m. p.  $252^\circ$ , the *l*-acid similarly gave a compound, m. p.  $238^\circ$ ,  $[\alpha]_D^{25} -27.25^\circ$ , and the *d*-acid a compound, m. p.  $238^\circ$  (corr.),  $[\alpha]_D^{25} +28.50^\circ$ . When diazotised and the product coupled with dimethylaniline, the *l*-acid gave a compound, m. p.  $189-190^\circ$ , and the *d*-acid a compound, m. p.  $188-189^\circ$ .

W. G.

**Catalytic Preparation of *o*-Toluidine.** C. O. HENKE and O. W. BROWNE (*J. Physical Chem.*, 1923, 27, 52-64).—In continuation of previous work on the catalytic reduction of nitrobenzene to aniline (A., 1922, i, 445, 535; ii, 833), the authors have investigated the catalytic reduction of *o*-nitrotoluene to *o*-toluidine by means of hydrogen. A nickel catalyst is too active for this purpose, a large part of the *o*-nitrotoluene being reduced beyond the toluidine stage. The highest yield obtained with nickel was 86.8%. Lead catalysts gave slightly higher yields of *o*-toluidine than of aniline, the respective yields in the two cases being 94.6% and 93.4%. Silver, when first used, gave a yield of 99% of *o*-toluidine, but its activity decreased with use, especially at the higher rates of flow of *o*-nitrotoluene. A 97% yield of *o*-toluidine was obtained with a copper catalyst used at  $260^\circ$ , the activity of which had been decreased by use at too high a temperature ( $300^\circ$ ). A copper catalyst prepared by the ignition of copper nitrate at  $415^\circ$  and containing 0.023% of iron gave a yield of 98.3% of *o*-toluidine at  $260^\circ$ . The corresponding yield of aniline was 91.9%. The activity of copper catalysts did not decrease with use. *o*-Nitrotoluene is more easily reduced than nitrobenzene.

J. S. G. T.

**The Isomerism of  $\beta$ -Benzylaminocrotonic Ester, its Reaction with Ferric Chloride, and that of Related Compounds.**

ERICH BENARY (*Ber.*, 1923, 56, [B], 53-55).—The constitutions  $\text{CH}_3\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{OEt}$  and  $\text{CH}_3\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  have been assigned by Rügheimer (A., 1916, i, 383) to the isomeric ethyl  $\beta$ -benzylaminocrotonates. The author considers this conception highly improbable, since it involves the enolisation of the carbethoxyl group in a series in which enolisation occurs only with difficulty and only when there is an accumulation of negative substituents around the carbon atom. The differing behaviour of the isomerides towards ferric chloride (Rügheimer, *loc. cit.*) is not directly related to their constitution, since the development of the coloration depends on their fission to base and ethyl acetoacetate. A similar dependence of the production of colour on the decomposition of the compound is observed in the cases of ethyl  $\beta$ -aminocrotonate, ethyl  $\beta$ -anilino (or *p*-toluidino)crotonate, methyl  $\beta$ -anilino crotonate, and ethyl ethylenediaminoacetoacetate, but not of their acidic derivatives as far as they have been examined. The colour is not developed if ferric acetate is substituted for ferric chloride.

It is doubtful whether the existence of two forms of ethyl

$\beta$ -benzylaminocrotonate is to be ascribed to *cis-trans*-isomerism or to structural isomerism. H. W.

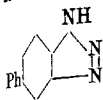
**The Tertiary Amines Derived from Benzhydrylamine.**

MARCEL SOMMELET (*Compt. rend.*, 1922, 175, 1149—1151; cf. A., 1922, i, 333).—The additive product of hexamethylenetetramine and diphenylbromomethane is converted by the action of formic acid into dimethylbenzhydrylamine,  $\text{CHPh}_2\cdot\text{NMe}_2$ , which combines very slowly in the cold with methyl iodide in methyl alcohol to give a *methiodide*, m. p. 211°. In hot solution, the hydriodide is obtained along with the methiodide and also a neutral, oily compound. Diethylbenzhydrylamine, benzhydrylpiperidine, and ethylbenzylbenzhydrylamine behave similarly towards methyl iodide, but in these cases very little, if any, of the methiodide is formed at 100°. If methyl bromide is used instead of methyl iodide, it is not possible to isolate any quaternary salt but only the hydrobromide. If dimethylbenzhydrylamine and methyl bromide are heated together in solution in methyl alcohol in a sealed tube at 100° for forty-eight hours, there is an abundant evolution of methyl ether, and benzhydryl methyl ether,  $\text{CHPh}_2\cdot\text{OMe}$ , and trimethylamine hydrobromide are obtained. If the methyl alcohol is replaced by butyl alcohol, the products are methyl butyl ether and benzhydryl butyl ether. These products may result as follows,  $\text{MeBr} + \text{MeOH} + \text{CHPh}_2\cdot\text{NMe}_2 = \text{Me}_2\text{O} + \text{CHPh}_2\cdot\text{NMe}_2\cdot\text{HBr}$ ;  $\text{CHPh}_2\cdot\text{NMe}_2\cdot\text{Br} = \text{CHPh}_2\cdot\text{Br} + \text{NMe}_3$ , and  $\text{CHPh}_2\cdot\text{Br} + \text{MeOH} + \text{NMe}_3 = \text{CHPh}_2\cdot\text{OMe} + \text{NMe}_3\cdot\text{HBr}$ . W. G.

**Diphenyl. III. Derivatives of Bromodiphenyl.** A. GARCÍA BANÚS and L. MEDRANO (*Anal. Fis. Quím.*, 1922, 20, 475—478; cf. A., 1922, i, 333).—By methylation of 4-bromo-4'-aminodiphenyl, using methyl alcohol and strong hydrochloric acid and heating in sealed tubes for ten hours at 140—150°, 4-bromo-4'-dimethylaminodiphenyl is obtained, which after recrystallisation has m. p. 205—208°. The mother-liquors from the crystallisation of this compound yield the corresponding *methochloride*, m. p. 180—185°. By nitration, 4-bromo-2-nitro-4'-dimethylaminodiphenyl is obtained; it forms large, orange-yellow plates, m. p. 107°. G. W. R.

**Diphenyl. III. Derivatives of Anilinodiphenyl.** A. GARCÍA BANÚS and J. GUITERAS (*Anal. Fis. Quím.*, 1922, 20, 479—485; cf. A., 1922, i, 333).—By boiling *p*-aminodiphenyl with fused sodium and 4:1:3-chlorodinitrobenzene in a reflux apparatus, 4-*op*-dinitroanilinodiphenyl,  $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , is obtained; it has m. p. 147° and crystallises in two forms, namely, orange needles from acetic acid and red crystals from toluene. The transformation point from the orange to the red form is 95—105°. By reduction with sodium sulphide, *p*-nitro-*o*-aminoanilinodiphenyl is obtained in platelets, m. p. 188°. 2-*op*-Dinitroanilinodiphenyl is crystalline, m. p. 159°. The corresponding 2-*p*-nitro-*o*-aminoanilinodiphenyl, obtained by reduction with sodium sulphide, forms dark orange platelets, m. p. 151—152°. 4'-Bromo-4-*op*-dinitroanilinodiphenyl from 4:4'-bromoaminodiphenyl forms yellow

leaflets, m. p. 204—205°. 3:4-Diaminodiphenyl gives, with hydrochloric acid and sodium nitrite, 5-phenylbenziminazole (annexed formula); it forms white plates, m. p. 154—155°. 4'-Amino-4-op-dinitroanilinodiphenyl forms small prisms, m. p. 245—247°. 4'-Amino-4-p-nitro-o-aminoanilinodiphenyl forms red platelets, m. p. 201°. 4'-Amino-4-op-diaminoanilinodiphenyl forms grey platelets, m. p. 197°.



G. W. R.

**The Preparation of Phenylimido-phosgene [Phenylcarbylamine Chloride] and the Chlorination of Formanilide.** R. S. BLY, G. A. PERKINS, and W. LEE LEWIS (*J. Amer. Chem. Soc.*, 1922, 44, 2896—2903).—Good yields of phenylthiocarbimide were obtained from thiocarbamilide by heating it under a reflux condenser for several hours with three parts of dilute sulphuric acid (one of acid to 2.5 volumes of water) and subsequently distilling the product with steam. When the thiocarbimide is chlorinated to saturation in solution in carbon tetrachloride or carbon disulphide, a 95% yield of phenylcarbylamine chloride is obtained if the solvent is removed directly by fractional distillation at a pressure of 30 mm. By using the phenylcarbylamine chloride itself as a solvent for subsequent chlorinations the other solvents could be dispensed with.

When formanilide was chlorinated in the cold with or without solvents in the presence of sulphur chloride the product was in all cases 2:4-dichloroformanilide. If the chlorination was conducted in the presence of thiophyl chloride, a series of products was obtained, namely, 2:4-dichloroformanilide, phenylcarbylamine chloride, *p*-chlorophenylcarbylamine chloride, b. p. 135—137°/30 mm., and 2:4-dichlorophenylcarbylamine chloride, b. p. 150—153°/30 mm. *p*-Chlorophenylcarbylamine chloride, when heated with glacial acetic acid, yielded *p*-chloroacetanilide, and with aniline yielded chlorotriphenylguanidine, m. p. 135—136°, as its hydrochloride, m. p. 247—250°. Similarly, 2:4-dichlorophenylcarbylamine chloride gave with acetic acid 2:4-dichloroacetanilide and with aniline 2:4-dichlorotriphenylguanidine, m. p. 129.5—130.5° (corr.) as its hydrochloride, m. p. 207—209° (corr.). The specific gravity of these substituted chlorides increases with the chlorine content but the lachrymatory effect diminishes.

W. G.

**New Derivatives of *p*-Phenethylcarbamide (Dulcin).** MAX BERGMANN, FRANZESKO CAMACHO, and FERDINAND DREYER (*Ber. Deut. pharm. Ges.*, 1922, 32, 249—258; cf. Speckan, A., 1922, 1, 580).—Various derivatives of dulcin (*p*-phenethylcarbamide) have been prepared in an effort to find one which should be more soluble while retaining the sweet taste. *a*-*p*-Phenethyl-*a*-methylcarbamide is more soluble and very sweet, but has a very persistent unpleasant flavour as well. The unpleasant taste is less marked in *a*-*p*-phenethyl-*a*-hydroxyethylcarbamide, but is still sufficient to render it technically useless. These and other compounds of the same type were prepared by the action of potassium cyanate on the hydrochlorides of the corresponding bases in aqueous solution. Derivatives of

dulcin in which an alkyl group is introduced into the primary amino-group are sparingly soluble and have no appreciable sweet taste. The latter compounds were prepared by the action of the corresponding thiocarbimides on phenetidine, whereby the thiocarbamide derivatives were formed, which were converted into the corresponding carbamide compounds by the action of mercuric oxide in acetic acid.

*a-p-Phenetyl-a-methylcarbamide*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$ , was obtained in good yield from potassium cyanate and *N*-methylphenetidine hydrochloride. It forms long needles, m. p. 128–129°. Similarly, *N*-hydroxyethyl-*p*-phenetidine gave *a-p-phenetyl-a-hydroxyethylcarbamide*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ , needles, m. p. 113–115°. Dihydroxypropylphenetidine (Ber., 1922, 55, 2796) gave *a-p-phenetyl-a-dihydroxypropylcarbamide*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}[(\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH})\cdot\text{CO}\cdot\text{NH}_2]$ , crystals, m. p. 138–139°, without sweet taste. By the action of ethyl chloroacetate on *p*-phenetidine, *p-phenetylglycine ethyl ester*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ,

is formed, leaflets, m. p. 33°, b. p. 152°/1 mm. (*amide*, m. p. 146°).

The ester is converted by potassium cyanate into *methyl-a-p-phenethylcarbamido-a-acetate*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NH}_2$ , colourless needles, m. p. 86–87°, of slightly bitter taste. With alcoholic ammonia it gives the corresponding *amide*, m. p. 236–237°, without distinctive taste.

*p*-Phenetidine and allylthiocarbimide gave *a-p-phenetyl-b-allylthiocarbamide*, crystals, m. p. 94–95°. With mercuric oxide, it gives *a-p-phenetyl-b-allylcarbamide*, crystallising from alcohol, acetic acid, or ethyl acetate in fine needles, from chloroform in rectangular plates, m. p. 157°.

Similarly, *a-p-phenetyl-b-methylthiocarbamide* crystallises from alcohol in truncated prisms, m. p. 128–128.5°, and *a-p-phenetyl-b-methylcarbamide* forms fine, long, quadrilateral platelets, m. p. 153°. *N*-Methyl-*p*-phenetidine and methylthiocarbimide give *a-p-phenetyl-ab-dimethylthiocarbamide*, truncated prisms, m. p. 99–100°, and *a-p-phenetyl-ab-dimethylcarbamide*, prisms, m. p. 94–95°. Similarly, *a-p-phenetyl-a-methyl-b-allylthiocarbamide* forms long needles, m. p. 68–69°, and *a-p-phenetyl-a-methyl-b-allylcarbamide*, thin needles, m. p. 57–58°. P. M.

**Hydrogenated Polycyclic Ring Systems. I. The Hydrogenation of Phenol and the By-products which are formed thereby.** WALTHER SCHRAUTH, WILHELM WEGE, and FRITZ DANNER (Ber., 1923, 56, [B], 260–268).—The hydrogenation of phenol in the gaseous state and under pressure has been studied in the presence of a nickel-copper catalyst. The arrangement of the apparatus for the first series of experiments is essentially that of Sabatier (*Die Katalyse*, 1914). Phenol is converted into a mixture of cyclohexanol (80–83%), cyclohexanone (6–9%), and smaller quantities of products of lower boiling point which have not been investigated fully; about 10% of the phenol remains unchanged. The results are closely similar to those obtained in

the presence of reduced nickel by Sabatier and Senderens (A., 1904, i, 156) and by Skita and Ritter (A., 1911, i, 272).

Hydrogenation under pressure in the presence of the nickel-copper catalyst is effected according to Schroeter's method (A., 1922, i, 122). It leads essentially to a mixture of cyclohexanol and cyclohexanone, containing about 9–14% of the latter. The volatile products formed during the hydrogenation in the vaporous phase are not observed, their place being taken by dark oils of high boiling point, the amount of which may rise to 10% when the action is unusually prolonged. A condensation appears therefore to occur in which cyclohexanol or more probably cyclohexanone takes part. Since the relative amounts of these substances is hereby undisturbed, it follows that the equilibrium between them is rapidly restored in the presence of the catalyst, which can also induce dehydrogenation (cf. Sabatier and Senderens, A., 1903, 393).

The liquids of high boiling point consist of di- and tri-cyclic condensation products consisting partly of saturated and partly of unsaturated ketones and aldehydes, which are readily converted by further hydrogenation into homogeneous saturated compounds of alcoholic character.

1:3-Dicyclohexylcyclohexane-2-one,  $C_6H_{11} \cdot C_6H_8O \cdot C_6H_{11}$ , long, colourless prisms, m. p. 131–132°, is obtained by the addition of alcohol to the least volatile fractions of the condensation products obtained by the hydrogenation of phenol under pressure. As in analogous cases, the presence of the ketonic group cannot be established by the help of semicarbazide hydrochloride or amino-uanidine hydrochloride, but the constitution of the product is placed beyond doubt by its production by the hydrogenation of 1:3-dicyclohexenylcyclohexane-2-one (cf. Mannich, A., 1907, i, 205). A solution of the ketone in methylcyclohexane is catalytically hydrogenated at 180–190° to a mixture of isomeric 1:3-dicyclohexylcyclohexane-2-ols, colourless needles, m. p. 117°, and a very viscous, colourless liquid, b. p. 220–221°/17 mm.; the latter is slowly converted into the solid variety when preserved. Either alcohol appears to be transformed into a mixture of the cis- and trans-acetate when acetylated. The liquid alcohol is dehydrated by zinc chloride at 200–210° with the formation of 1:3-dicyclohexyl-Δ<sup>1</sup>-cyclohexene, b. p. 204–207°/15 mm.,  $d_{20} 0.9525$ ; the hydrocarbon is also preparable from the solid alcohol, but it is uncertain whether a uniform product is obtained in this manner. It is transformed by hydrogenation in the presence of methylcyclohexane to a mixture of 1:3-dicyclohexylcyclohexanes, long, colourless needles, m. p. 66–67°, and a liquid, b. p. 192–196°/12 mm.,  $d_{20} 0.9335$ .

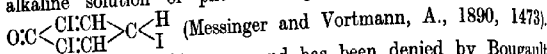
H. W.

**The Synthesis of Phosphoric Acid Esters. I.** SHIGERU MATSU and SHINICHIRO KUMAMOTO (*Mem. Coll. Sci. Kyoto*, 1922, 6, 45–48).—cycloHexanol when left in contact with phosphoric acid in presence of phosphoric oxide forms a mono-ester,  $\frac{1}{2}H_{11}H_2PO_4$ , colourless crystals, m. p. 77–78°. The soluble VOL. CXXIV. i.

barium salt,  $C_6H_{11}BaPO_4$ , is a white, crystalline substance; the silver salt is insoluble in water. When heated, the free ester and the barium salt are both decomposed into cyclohexene and phosphoric acid or phosphate. The di- and tri-cyclohexyl phosphates could not be obtained.

E. H. R.

**The Action of Iodine on Alkaline Solutions of Phenol.**  
G. VORTMANN (*Ber.*, 1923, 56, [B], 234—246).—In a previous communication it has been shown that iodine reacts with an alkaline solution of phenol to give "di-iodophenol iodide,"



The existence of this compound has been denied by Bougault (A., 1908, ii, 738), by Wilkie (A., 1911, ii, 546; 1912, i, 346), and by Hunter and Woollett (A., 1921, i, 238). Its isolation is now described.

The action of iodine on an alkaline solution of phenol takes place by the initial substitution of the halogen for the sodium atom of the phenoxide and its subsequent migration into the nucleus:  $Ph \cdot O \cdot I \rightarrow C_6H_4I \cdot OH$ . The process is then repeated until tri-iodophenol is produced. Even in the presence of a large excess of iodine, the nature of the product depends essentially on the quantity of alkali. Iodination therefore is effected by the alkali hypiodite. Even in the presence of more than three molecular proportions of sodium hydroxide a compound more highly iodinated than tri-iodophenol is not produced; if the solution is acidified after not more than five minutes, this compound is quantitatively precipitated and is not further affected by the presence of much free iodine in the acid medium. If the phenol solution is not too dilute, tri-iodophenol separates previously to acidification; if it is shaken from time to time in the alkaline suspension, it gradually darkens in colour and passes into a mixture of "di-iodophenol iodide" and tetraiododiphenylenequinone (cf. Lautemann, *Annalen* 1861, 120, 309). Iodination of phenol in the presence of a large excess of alkali yields only di-iodophenol.

Di-iodophenol iodide is most conveniently prepared by the prolonged action of cold sodium hypiodite solution on phenol. The brown mixture of the product with Lautemann's red is treated with acetone in which the former only is soluble to a yellowish-brown solution from which it is reprecipitated by the addition of much water and sodium chloride in the form of irregular dark violet-brown leaflets or scales, m. p. 122°. It slowly loses iodine when exposed to air and gives a violet coloration when its dilute solution in acetone is treated with a little sodium thiosulphate solution.

The mechanism of the formation of Lautemann's red is discussed in detail and appears to be represented by the following equations:  $C_6H_2I_3 \cdot OH + NaIO = C_6H_2I_3 \cdot OI + NaOH$ ;  $C_6H_2I_3 \cdot OI \rightarrow C_6H_2I_2(O) \cdot I_2$ ,  $C_6H_2I_2(O) \cdot I_2 + NaOH = C_6H_2I_2(O) \cdot HI + NaO$ ;  $2C_6H_2I_2(O) \cdot HI = 2HI + O \cdot C_6H_2I_2 \cdot C_6H_2I_2 \cdot O$ .

Oxidation of tri-iodophenol by the requisite amount of potassium

persulphate in the presence of sodium carbonate gives a mixture of di-iodophenol iodide and Lautemann's red. Reduction of the latter in glacial acetic acid solution by stannous chloride and hydrochloric acid gives a colourless compound which appears to be a hydrogenated derivative (cf. Hunter and Woollett, *loc. cit.*).

Phenol may be estimated by treating its solution, which must contain at least four molecular proportions of sodium hydroxide, with an excess of iodine solution; after five minutes the solution is acidified with dilute sulphuric acid, whereby tri-iodophenol is precipitated. The excess of iodine is estimated in an aliquot portion of the supernatant liquor. If the time of action is prolonged beyond five minutes, the precipitate is more or less discoloured, but the consumption of iodine is not thereby changed. H. W.

**The Decomposition of Ethers by Metallic Sodium.** PAUL SCHORIGIN (*Ber.*, 1923, 56, [B], 176—186; cf. A., 1910, i, 547).—Diphenyl ether reacts exothermally with sodium wire at 180—200°, giving phenol (60—75%), benzene (30%), a small quantity of diphenyl, phenol-like products of high boiling point, and carbonised substances. The reaction also occurs in the presence of neutral solvents of suitable boiling point. The reaction is considered to involve the primary addition of sodium to yield the product  $\text{Ph}_2\text{ONa}_2$ , and immediate scission of the latter into sodium phenoxide and sodium phenyl. The latter is decomposed by water (evolved during the production of the complex, pitch-like products) with the formation of benzene and sodium hydroxide. The formation of diphenyl may be ascribed to the direct removal of oxygen from the ether by sodium or to the interaction of sodium phenoxide and sodium phenyl,  $\text{PhNa} + \text{PhONa} = \text{Ph} \cdot \text{Ph} + \text{Na}_2\text{O}$ . The intermediate formation of organo-metallic sodium derivatives is rendered probable by the observation that an extremely vigorous action takes place when dry air is bubbled through the mixture, but, on the other hand, salicylic acid is produced when carbon dioxide is introduced into it, whereas sodium phenyl would be expected to yield benzoic acid.

$\alpha$ -Naphthyl ethyl ether reacts vigorously with sodium at 230—270°, yielding naphthalene,  $\alpha$ -naphthol, carbonised and pitch-like products, ethylene, ethane, and hydrogen. The volume of ethylene formed exceeds that of ethane; the production of butane or butylene could not be established.  $\beta$ -Naphthyl ethyl ether reacts more energetically than the  $\alpha$ -isomeride with sodium, but yields similar products, naphthalene,  $\beta$ -naphthol, ethylene, ethane, and hydrogen. Phenetole does not react to an appreciable extent with sodium at any temperature below its boiling point. At 200—260°, it becomes decomposed into phenol, ethane, ethylene, hydrogen, products of high boiling point, carbonised material, and small quantities of ethyl alcohol. The intermediate formation of organo-metallic substances is established by the observations that the product of reaction becomes heated, sometimes to the point of ignition, when exposed to air, and that propionic acid is produced when it is treated with carbon dioxide.

Benzyl ethyl ether reacts with sodium at 140°, this temperature being much below its boiling point; benzyl alcohol appears to be produced, but owing to an accident, the products could not be fully investigated. isoAmyl ether yields small amounts of isoamylic alcohol when heated with sodium at 200–220° and subsequently at 235–275°.

The experiments show that the desiccation of simple ethers by distillation over sodium is open to suspicion, and that the process is quite unsuitable for fatty-aromatic and aromatic ethers of high boiling point. If the use of sodium is desired, milder conditions should be adopted, and the metal should be removed previously to the distillation of the ether.

H. W.

**Simplified Methods of Preparing certain Organic Substances. I. Nitrophenetoles and Nitroanisoles.** H. VAN ERP (*Ber.*, 1923, 56, [B], 217–221).—The substances are prepared by the action of potassium alkyl sulphates on potassium nitrophenoxides in the presence of a small quantity of glycerol. The latter, after being purified and dehydrated by distillation under diminished pressure, is placed in a  $\frac{1}{2}$ -litre flask provided with a reflux condenser filled with cold water, but with both tubes closed; an intimate mixture of the potassium compounds, previously desiccated at 140° and 100°, respectively, is added; and the mixture is heated in an oil-bath, usually at about 180° to 210°, until the change appears to be complete. The yields obtained are as follows: *o*-nitrophenetole, above 90%; 2:4-dinitrophenetole, 56%; 6-chloro-2:4-dinitrophenetole, 0%; *p*-nitroanisole, 87%.

Contrary to the statements in the literature, pure methyl sulphate has b. p. 76°/15 mm.,  $d_{15}^{15}$  1.3348.

Contrary to statements in Beilstein's *Handbuch*, crystalline potassium methyl sulphate is anhydrous and not deliquescent.

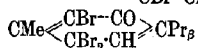
H. W.

**Certain Bromine Derivatives of Thymol.** HANS JOST and FRIEDRICH RICHTER (*Ber.*, 1923, 56, [B], 119–123).—The action of bromine on thymol dissolved in glacial acetic acid has been examined by Dannenberg (*A.*, 1903, i, 338), who has thereby isolated a product which he considers to be the 'keto-bromide',  $\text{CMe} \begin{smallmatrix} \text{CBr} \cdots \text{CO} \\ \text{CHBr} \cdots \text{CH} \end{smallmatrix} \text{CPr}^6$ . The remarkable constitution of the compound has led the authors to re-examine the reaction; they draw the conclusion that the substance described by Dannenberg does not exist.

The action of bromine on thymol under the conditions adopted by Dannenberg proceeds beyond the formation of a dibromo-compound, and gives also a true keto-bromide,  $\text{C}_{10}\text{H}_{11}\text{OBr}_2$  (see later), which renders the product of the reaction incompletely soluble in solutions of alkali hydroxide; if a smaller proportion of bromine is used, its production is avoided and the dibromo-thymol is completely soluble; it crystallises in long, colourless prisms, m. p. +3.5–4°, b. p. 160–161°/16 mm., 175°/25 mm.

$d_{4}^{25}$  1.6631,  $d_{4}^{25}$  1.6618,  $d_{4}^{25}$  1.6588; the corresponding benzoate forms small, colourless needles, m. p. 89–90°, whereas Dannenberg gives m. p. 80–81°.

Thymol is converted by a solution of calcium bromohypobromite into tribromo-*p*-menthadienone,  $\text{CMe} \begin{smallmatrix} \text{CBr}_2 \cdot \text{CO} \\ \text{CBr} \cdot \text{CH} \end{smallmatrix} \text{CPr}^s$  or



(see above), large, dark yellow plates, m. p. 59–60° after softening at 55°. The substance decomposes somewhat readily when preserved. It liberates two atomic proportions of iodine from neutral potassium iodide solution, and is reduced by stannous chloride in the presence of hydrogen chloride and acetic acid to dibromothymol. It is converted by cold, concentrated sulphuric acid into 2:4:6-tribromo-*m*-cresol, its behaviour in this respect being similar to that of trichloro-*p*-menthadienone (Crowther and McCombie, T., 1913, 103, 539, 545). The keto-bromide is also obtained by the action of sodium hypobromite or of an excess of bromine on thymol. When dissolved in carbon tetrachloride and shaken with aqueous potassium hydroxide solution (4%), it is transformed into a brown, amorphous powder, m. p. 220–230° (decomp.) after darkening at 200°. H. W.

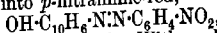
#### Amino-alcohols of Tetralin [Tetrahydronaphthalene].

A. GONZÁLEZ and M. CAMPOY (*Anal. Fis. Quim.*, 1922, 20, 534–538).—By the action of hypobromous acid on 1:4-dihydronaphthalene, 3-bromo-2-hydroxytetrahydronaphthalene is obtained. It is crystalline, and has m. p. 107°. By acting on it with anhydrous dimethylamine in benzene solution in a sealed tube at 120°, 2-dimethylamino-2-hydroxytetrahydronaphthalene is obtained, b. p. 65–170°/14 mm. 2-Dimethylamino-1-hydroxytetrahydronaphthalene has b. p. 157–158°/13 mm. The following compounds were also prepared: 2-benzoyl-3-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 228°; 2-valeryl-3-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 173°; 2-cinnamoyl-3-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 178°; 2-pyruvoyl-3-dimethylaminotetrahydronaphthalene hydrochloride; 1-benzoyl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 176°; 1-valeryl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 65°; 1-cinnamoyl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 176.5°; 1-pyromucyl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 172°. Hydrochlorides of the 1:2-series are more soluble and have a lower melting point than those of the 1:3-series. G. W. R.

#### A New Class of Derivatives of $\beta$ -Naphthol, the 1-Aryl-

amino- $\beta$ -naphthols. A. WAHL and ROBERT LANTZ (*Bull. Soc. Chim.*, 1923, [iv], 33, 93–110).—Certain atoms and groups which in the benzene nucleus are only displaced at high temperatures or not at all are extremely reactive when substituted in the  $\alpha$ -position of  $\beta$ -naphthol. Thus the sulphonic group of  $\beta$ -naphthol- $\alpha$ -sulphonic acid is eliminated when the substance is treated in aqueous solution

with *p*-nitrobenzenediazonium chloride. In alkaline solution, the reaction occurs in two stages with the intermediate formation of an extremely unstable compound, which is thought to be a diazo-oxide of the formula  $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . In presence of the least trace of acid, this yellow, water-soluble substance is instantly converted into *p*-nitraniline-red,



with liberation of sulphuric acid. With  $\alpha$ -chloro- $\beta$ -naphthol, the intermediate product cannot be isolated, the dye being produced at once with the elimination of the chlorine atom. The mobility of the halogen atom in the  $\alpha$ -position is further illustrated by the action of sodium sulphite in weak alcoholic solution,  $\beta$ -naphthol being formed and the halogen eliminated.  $\alpha$ -Chloro- or  $\alpha$ -bromo- $\beta$ -naphthol also reacts vigorously with primary aromatic amines, and, moderating the reaction by using a large excess of the amine, quantitative yields of 1-arylamino-2-hydroxynaphthalenes are obtained. 1-Anilino- $\beta$ -naphthol forms white needles, m. p. 155–156°, which darken on exposure to air. The hydrochloride forms a white, crystalline powder, and the methyl ether colourless needles m. p. 82–83°. 1-p-Toluidino- $\beta$ -naphthol forms white prisms m. p. 138–139°, and its methyl ether white needles, m. p. 94°. 1-o-Toluidino- $\beta$ -naphthol, crystallised from acetic acid, melts at 114–115°. 1-o-Anisidino- $\beta$ -naphthol crystallises in small needles, m. p. 110°. 1-o-Methoxy-m-toluidino- $\beta$ -naphthol forms white needles, m. p. 118°. 1- $\alpha$ -Naphthylamino- $\beta$ -naphthol forms grey needles, m. p. 171°, and the corresponding  $\beta$ -derivative a grey powder, m. p. 166–167°. G. F. M.

**The Influence of Boric Acid on some Polyhydroxy-derivatives of Naphthalene and Anthraquinone.** J. BÖSEKEN [with (MLLE) K. C. ANEMA and (MLLE) M. A. J. BREVET] (*Ra. trav. chim.*, 1922, 41, 778–783; cf. A., 1915, ii, 667).—Two *o*-dihydroxynaphthalenes, similarly to dihydroxyphenols (cf. Böseken and Van Rossem, A., 1912, ii, 147), considerably increase the electrical conductivity of solutions of boric acid, but the increase due to the 2:3-dihydroxy-compound is much greater than that conferred by its 1:2-isomeride. This difference is attributed to greater freedom of the hydroxyl groups in the former compound. The hydroxy-derivatives of anthraquinone were found to be insufficiently soluble in water for similar measurements of conductivity to be made, but a coloration was observed in each case on the addition of boric acid to a solution of the substance in dilute alcohol. The suggestion is made that the coloration depends on the presence of two hydroxyl groups in the ortho-position with respect to each other, or, alternatively, that it is correlated with the presence of a hydroxyl group next to a carbonyl group.

H. J. E.

**Preparation of Benzyl Esters of some Acids of High Boiling Point.** T. J. THOMPSON and GERALD J. LEUCK (*J. Amer. Chem. Soc.*, 1922, 44, 2894–2896).—Benzyl esters of certain

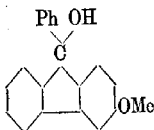
acids which boil at above 100° without decomposition have been prepared by heating together the alcohol and acid in the requisite proportions in a flask fitted with an air condenser of such a length that the benzyl alcohol vapour condenses just below its upper end, whilst it is not long enough to cause the condensation of the water vapour arising from the interaction of the alcohol and acid. Pure benzyl alcohol, free from traces of benzaldehyde, must be used. Good yields were obtained in the case of eight esters, but in two cases it was necessary to vary the pressure in the flask. Other high boiling point alcohols were tried instead of benzyl alcohol, but they did not give satisfactory results.

W. G.

**Triphenylmethyl. XXXII. *p*-Benzyloxy- and *p*-Methoxytriphenylmethyl.** M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1923, 45, 207—222).—*p*-Benzyloxytriphenylcarbinol, m. p. 94°, was prepared from the corresponding hydroxy-compound by the Schotten-Baumann reaction. When reduced with zinc and acetic acid, it yielded *p*-benzyloxytriphenylmethane, m. p. 116·5°, and with hydrogen chloride gave *p*-benzyloxytriphenylmethyl chloride, m. p. 77°, from which, by the action of sodium ethoxide, *p*-benzyloxytriphenylmethyl ethyl ether, m. p. 89°, was obtained. *p*-Benzyloxytriphenylmethyl bromide had m. p. 90°. When the chloride was shaken with molecular silver in dry benzene, *p*-benzyloxytriphenylmethyl, m. p. 142—145°, was obtained; it rapidly absorbed oxygen from the air, giving a *peroxide*, m. p. 171°, and absorbed iodine from its solution giving an unstable *iodide*. In benzene solution, the free radicle reacts with hydrogen chloride to give a mixture of the carbanyl chloride and the triarylmethane, and these interact only to a very slight extent to give a dialkyloxy-*p*-benzhydryltetraphenylmethane. A benzene solution of the free radicle exposed in a quartz tube to sunlight undergoes auto-oxidation and reduction to form a biphenylene free radicle and *p*-benzyloxytriphenylmethane. The free radicle was crystallised from a number of different types of solvents, but only in one case, namely, with ether, was an additive compound formed. The degree of dissociation of di-*p*-benzyloxyhexaphenylethane in six different solvents over a temperature range from -17° to +53° and in concentrations from 1 to 6%, was found to vary from 26 to 56% with the concentration, the temperature, and the nature of the solvent.

*p*-Methoxytriphenylcarbinol gave a chloride and a bromide, m. p. 143°, and from the chloride the free radicle *p*-methoxytriphenylmethyl, m. p. 145—150°, was obtained. It absorbs oxygen, giving a *peroxide*, m. p. 157°, and iodine, giving an *iodide*. Like the benzyloxy-compound, the main reaction with hydrogen chloride in benzene solution is to yield the carbanyl chloride and the triarylmethane. When exposed to sunlight in the same solvent a mixture of *p*-methoxytriphenylmethane and a biphenylenetriarylmethyl result, and from this solution on exposure to air 9-phenyl-3-methoxyfluorenyl *peroxide*, m. p. 200° (decomp.), was obtained. This peroxide was synthesised by a different method as follows:

3-methoxy-9-fluorenone was converted by the action of magnesium phenyl bromide into the *carbinol* (annexed formula), m. p. 84°, giving a *chloride*, m. p. 119°. From this by shaking with molecular silver the free radicle was obtained, and this on exposure to air gave the required peroxide. *p*-Methoxy-triphenylmethyl did not give any additive compounds with the various solvents tried. The degree of dissociation of di-*p*-methoxyhexaphenylethane, determined as in the case of the benzyloxy-compound, varied from 22 to 42%.



W. G.

**Triphenylmethyl. XXXI. Tautomerism of *o*-Hydroxy-triphenylcarbinol; *o*-Hydroxy- and Alkyloxy-triphenylmethyl.** M. GOMBERG and D. NISHIDA (*J. Amer. Chem. Soc.*, 1923, 45, 190—207).—When *o*-hydroxytriphenylcarbinol in solution in glacial acetic acid, carbon tetrachloride, benzene, toluene, or xylene is warmed, the solution becomes brown, the coloration beginning at 50—80°, according to the nature of the solvent, and increasing in intensity with rise in temperature or concentration of the solution. This coloration is due to tautomerisation of the carbinyl to the quinonoid form, and the change is reversible if the temperature does not exceed 110°. Above 110°, the carbinol, in solution, slowly loses water and yields, not the expected *o*-fuchsonone, but a rearrangement product, namely, 9-phenylxanthane. The carbinyl chloride undergoes similar changes, but at much lower temperatures, and loses hydrogen chloride instead of water. *o*-Benzyloxytriphenylcarbinyl chloride is considerably more stable than the *o*-hydroxy-compound, but even at ordinary temperatures it undergoes a gradual spontaneous decomposition. *o*-Hydroxy-, *o*-benzyloxy-, and *o*-methoxy-triphenylcarbinyl chlorides are all decomposed by molecular silver, giving the free radicle, but in the cases of the first two the free triarylmethyls could not be isolated owing to secondary changes, but *o*-methoxytriphenylmethyl was isolated and its physical and chemical properties were determined. It exists in solution in the unimolecular state to the extent of 26—49%, depending on the temperature. At ordinary temperatures only about one-third of the total amount of the unimolecular triarylmethyl is in the quinonoid state, the remaining two-thirds being benzenoid.

*o*-Hydroxytriphenylchloromethane was obtained by dissolving the carbinol in ether, adding calcium chloride, and saturating the solution with hydrogen chloride. Colourless crystals were obtained which rapidly became brown even in a desiccator. When shaken in benzene solution with molecular silver in the presence of air the polymerised *o*-hydroxytriphenylmethyl, m. p. 237°, was obtained together with a peroxide,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{O}\cdot\text{O}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , m. p. 131°. *o*-Benzyloxytriphenylcarbinol, m. p. 172°, was prepared from the hydroxy-compound, and gave the carbinyl chloride, m. p. 146°, which with molecular silver gave the polymeride, m. p. 207°, the triarylmethyl, and also a peroxide, m. p. 153°.

*o*-Methoxytriphenylcarbinol gave a stable chloride and bromide, m. p. 127—128°. The chloride when decomposed by molecular silver gave a mixture of *di-o-methoxyhexaphenylethane*, m. p. 117—121°, and *o-methoxytriphenylmethyl*. The free radicle, when exposed to air, rapidly absorbs oxygen and gives its *peroxide*, m. p. 160—161° (decomp.), and, similarly, it absorbs iodine to give its *iodide*. Both the free radicle and its chloride and bromide show decided electrical conductivity in liquid sulphur dioxide. W. G.

**Pinacolic and Semi-pinacolic Transpositions. Comparative Migratory Aptitudes of Different Radicles.** M. TIFRENEAU and (MILLÉ) J. LEVY (*Compt. rend.*, 1923, 176, 312—314).—From examples of pinacolic and semi-pinacolic transpositions of substituted glycols and iodohydrins quoted, it is shown that ethyl and benzyl groups have a much more marked aptitude for migration than has the methyl group, and in many cases the migration of the former groups is exclusive. W. G.

**Compounds containing the Trimethylene [*cyclo*Propane] Ring.** P. BRUYLANTS and A. STASSENS (*Bull. Acad. roy. Belg.*, 1921, 702—719).—*cyclo*Propanecarboxylonitrile, when prepared from  $\gamma$ -chlorobutyronitrile by distilling with dry potassium hydroxide, contains crotono- or isocrotono-nitrile. The pure *cyclo*-nitrile boils at 134—134.2°/762.5 mm. Pure *cyclo*propanecarboxylic acid has m. p. 18.1° and b. p. 181.8—182.0°/766 mm. The corresponding chloride, on chlorination, at the b. p. gives (a) 1-chlorocyclopropanecarboxyl chloride, b. p. 141—143°,  $d_4^{20}$  1.336,  $n_D^{20}$  1.4759, and (b) a small amount of what is apparently  $\alpha$ -dichlorobutyl chloride, b. p. 212—214°. The former (a) was converted by water into 1-chlorocyclopropanecarboxylic acid, colourless needles, m. p. 70—71°, b. p. 206°; sodium salt, colourless, hygroscopic needles; methyl ester, b. p. 152—153°/761 mm.,  $d_4^{20}$  1.179; ethyl ester, b. p. 65—66°/15 mm. or 162—163°/762.5 mm.,  $d_4^{20}$  1.126,  $n_D^{20}$  1.4417; amide, white crystals, m. p. 131—132°.

Ethyl 1-chlorocyclopropanecarboxylate by treatment with magnesium methyl bromide is converted into a *chlorohydrin*,  $C_3H_5Cl.CMe_2.OH$ . The latter has b. p. 156.5—157°/756 mm.,  $d_4^{20}$  1.065, forms an *acetyl* derivative,  $d_4^{20}$  1.086, and is almost unaffected by hot aqueous potassium hydroxide.

The chlorine atom in 1-chlorocyclopropanecarboxylic acid is not reactive enough to permit of the preparation of derivatives by its replacement. The constitution of the acid was decided from conductivity measurements with the acid and its sodium salt, whence the dissociation constant (100 *k*) was found to be between 0.05 and 0.06, a value only to be explained if the chloro-group is in the  $\alpha$ -position.

By treating the higher boiling fractions of the above chlorination with methyl alcohol in presence of a little sulphuric acid, methyl  $\alpha$ -chlorocyclopropanecarboxylate and methyl  $\alpha$ -dichlorobutylate, b. p. 212—214°, were obtained.

The molecular heats of combustion of *cyclo*propanecarboxylic

acid at constant volume and at constant pressure were found to be 486.1 and 486.4 cal., respectively, whereas for crotonic acid the value is 478.0 cal. The heat of formation of the acid in the liquid state is 97.8 cal. (crotonic acid, 102.3 cal.).

Determinations of the viscosities and melting points of mixtures of cyclopropanecarboxylic acid with water are described, and point to the existence of a hydrate,  $C_3H_6O_2 \cdot H_2O$ .

E. E. T.

**4-Fluoro-3-nitrobenzoic Acid.** H. ROUCHE (*Bull. Acad. roy. Belg.*, 1921, 534—547).—4-Fluorobenzoic acid, on treatment with nitric acid ( $d$  1.495), is converted to the extent of 80% into 4-fluoro-3-nitrobenzoic acid, white needles, *m. p.* 121.5°, 4-fluoronitrobenzene also being formed as the result of the displacement of the carboxyl group by the nitro-group. The new acid forms soluble and highly coloured salts (alkali metals, red; alkaline-earth metals, yellow or orange). The silver salt is unstable. The ethyl ester, yellow crystals, melts at 45.3°. The chloride, *b. p.* 210°/130 mm., on treatment with aqueous ammonia, gives 3-nitro-4-aminobenzamide, dry ammonia in ethereal solution, however, giving 4-fluoro-3-nitrobenzamide, a waxy mass, *m. p.* 153°.

The solubilities of 4-fluoro-, 4-chloro-, and 4-bromo-3-nitrobenzoic acids have been compared.

The dissociation constants (100 *k*) of 4-fluoro- and 4-chloro-3-nitrobenzoic acids were found to be respectively 0.0433 and 0.048 (cf. A., 1890, 1209), the corresponding 4-bromo-acid being stronger than these two acids. *p*-Fluorobenzoic acid, used in comparison, gave 100 *k* 0.00735. Owing to the labile nature of the fluoro-group in fluoronitrobenzoic acid, conductivity determinations with the latter were carried out in presence of hydrochloric acid.

A study of the velocities of reaction with sodium methoxide of sodium fluoronitrobenzoate and *o*-fluoronitrobenzene showed that the carboxyl group renders a para-fluoro-group more labile.

E. E. T.

#### **$\alpha$ -Nitrophenylacetamide and some of its Derivatives.**

A. J. VAN PESKI (*Rec. trav. chim.*, 1922, 41, 687—700; cf. A., 1909, i, 647).—On treatment of  $\alpha$ -isonitrophenylacetamide with concentrated sodium hydroxide solution, the sodium derivative of the amide which is first formed gradually disappears and sodium nitrophenylacetamide is formed. This reacts with bromine to give  $\alpha$ -bromo- $\alpha$ -nitrophenylacetamide, which is easily obtained pure. The action of dilute sulphuric acid on the aqueous solution of the sodium derivative gives a white precipitate which becomes viscid and then solidifies. This consists of  $\alpha$ -nitrophenylacetamide, which on crystallisation from benzene or chloroform is obtained in the form of white needles, *m. p.* 82.5—83°. These remain unchanged for a considerable time; decomposition may be detected by a lowering of the melting point, and after some months the substance is transformed into a thick brown syrup. Complete decomposition may be effected in less than two hours by heating

on the water-bath : among the decomposition products are nitro-gen, nitrous oxide, phenylglyoxylic acid, phenylglyoxylamide, benzonitrile, water, and two unidentified derivatives of phenylglyoxylamide. On boiling in contact with water, the products are phenylglyoxylic acid and its amide, benzoic acid and the oxime of phenylglyoxylamide. The chloro-derivative of  $\alpha$ -nitrophenylacetamide is prepared in a similar manner to the bromo-derivative, but the corresponding iodine compound is obtained in ethereal solution of iodine by reaction with the silver salt of the amide. All three halogen derivatives liberate nitric oxide and the halogen on being heated; the decomposition may take place explosively. The following descriptions are given :  $\alpha$ -chloro- $\alpha$ -nitrophenylacetamide, white prisms, m. p. 107–115°;  $\alpha$ -bromo- $\alpha$ -nitrophenylacetamide, crystals, m. p. 108–116°;  $\alpha$ -iodo- $\alpha$ -nitrophenylacetamide, yellow, rod-shaped crystals, m. p. 97–100°; *o*-bromo- $\alpha$ -nitrophenylacetamide, white, rod-shaped crystals, m. p. 125°; *p*-bromo- $\alpha$ -nitrophenylacetamide, white, rod-shaped crystals, m. p. 101.5°; ethyl imidophenylperacetate,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{O}\cdot\text{OEt}$ , small, rod-shaped crystals, m. p. 180°.

H. J. E.

**Asymmetrical Synthesis.** EMIL ERLÉNMEYER and HANS ERLÉNMEYER (*Biochem. Z.*, 1922, **133**, 52–62).—If bromine be added to a solution containing cinnamic acid, a sugar, and a zinc salt, the dibromophenylpropionic acid formed is optically active, except in the case of lactose, where the resulting acid is inactive. Presumably a complex salt of zinc with cinnamic acid on the one hand, and with the sugar on the other, is formed, and this optically active compound adds on bromine asymmetrically. With dextrose, levulose, and sucrose excess of the  $l$ - $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid is formed, and with *l*-arabinose excess of the *d*-acid. Levulose is particularly effective, and it is likewise active if  $\alpha$ -methylcinnamic acid is used instead of cinnamic acid.

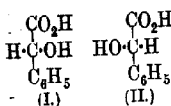
W. O. K.

**The Iodination of *m*-Hydroxybenzoic Acid.** P. H. BEIJER (*Rec. trav. chim.*, 1922, **41**, 701–702).—Monoiodohydroxybenzoic acid was prepared by Wieselsky's method (*Annalen*, 1874, **174**, 405). An identical acid was obtained from 4-nitro-3-hydroxybenzoic acid by reduction of the nitro-group, diazotisation, and treatment with potassium iodide. The acid is thus 4-iodo-3-hydroxybenzoic acid, so that the action of iodine yields a derivative substituted similarly to that obtained on bromination. This was confirmed by the preparation of 6-iodo-3-hydroxybenzoic acid cf. Lüppricht, A., 1891, 1036) which is not identical with the acid obtained by Wieselsky.

H. J. E.

**The Configuration of Mandelic Acid and other  $\alpha$ -Hydroxyacids.** KARL FREUDENBERG, FRITZ BRAUNS, and HEINRICH ENGEL (*Ber.*, 1923, **56**, [B], 193–200).—The hypothesis that the optical activity of similarly constituted substances of the same configuration is influenced in a uniform manner by change of temperature, dilution, or addition of neutral salts has led Clough

(T., 1918, 113, 526) to assign *l*-mandelic acid to the *d*-series (configuration I), whereas Hudson (A., 1918, i, 292), on the consideration that all hydroxy-acids which yield dextrorotatory amides and hydrazides belong to the *d*-series, has assigned to it the configuration II (*l*-mandelic acid is levorotatory). *l*-Hexahydromandel-



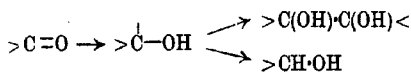
amide has now been prepared, and shown to be strongly dextro-rotatory. Since, therefore, *l*-mandelic and *l*-hexahydromandelic acids are configurationally related, Hudson's rule appears to be broken. A consideration of the optical activities of  $\alpha$ -hydroxy-acids of known configuration and of their amides confirms the validity of Clough's deductions. Hudson's rule appears merely to require a slight modification in the sense that  $\alpha$ -hydroxy-acids are considered to belong to the *d*-series when their specific rotation is displaced in the dextro-direction on conversion into the amide. An actual transition from *l*avo to dextro is only observed with substances of low rotatory power, such as the monocarboxylic acids of the sugar group, from a study of which the rule was first developed.

*dl*-cycloHexylglycollic acid, m. p. 134—135° [Godehot (A., 1910, i, 480) gives 130—131°], is prepared by the catalytic hydrogenation of *dl*-mandelic acid in aqueous solution in the presence of platinum with gum arabic or gelatin as protective colloid. It is smoothly esterified to *methyl dl*-cyclohexylglycolate, b. p. 122—123°/18 mm., from which the corresponding amide, m. p. 156° (Godehot gives m. p. 155°) is prepared. *dl*-cycloHexylglycolphenylhydrazide has m. p. 213°. *d*(-)-cycloHexylglycollic acid, prepared by hydrogenation of *l*-mandelic acid, has m. p. 128—129°,  $[\alpha]_{\text{D}}^{25}$  yellow -26.6°,  $[\alpha]_{\text{D}}^{25}$  yellow -25.8° in glacial acetic acid solution. The corresponding *methyl* ester has b. p. 123°/19 mm.,  $[\alpha]_{\text{D}}^{25}$  yellow -4.7°; the *phenylhydrazide*, m. p. about 215° (decomp.),  $[\alpha]_{\text{D}}^{25}$  yellow +55.25° in glacial acetic acid, and the *amide*, m. p. 158°,  $[\alpha]_{\text{D}}^{25}$  yellow +47.4° in alcohol,  $[\alpha]_{\text{D}}^{25}$  yellow +41.16° in aqueous (20%) alcohol are described.

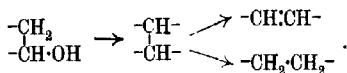
*d*(-)-Lactic acid, prepared by the resolution of the *r*-acid with morphine (cf. Irvine, T., 1906, 89, 935), is converted into the *methyl* ester, b. p. 50—60°/25 mm.,  $[\alpha]_{\text{D}}^{20}$  yellow +7.3°, and thence into the *amide*, m. p. 49—51°,  $[\alpha]_{\text{D}}^{25}$  yellow +22.2°; it is remarkable that the active amide is very deliquescent and that this property is not shared by the *r*-amide. H. W.

**The Theory of Reduction. The Reduction of the Carbonyl Group by Zinc Amalgam.** WILHELM STEINKOPF and ARTHUR WOLFRAM (*Annalen*, 1923, 430, 113—161).—A careful study of the action of zinc amalgam and aqueous or alcoholic hydrochloric acid on a variety of carbonyl compounds has shown that product of several distinct types may be obtained, and that the formation of these may be accounted for by ascribing to the process the following general mechanism. In the first place, hydrogen becomes attached to the oxygen of the carbonyl group, giving a radical (containing trivalent carbon) which may react either with

itself, yielding a pinacone or with more hydrogen, forming an alcohol :



secondly, if the alcohol contains a  $CH_2$  residue next to the carbinol group, water may be eliminated, giving first a compound containing two tervalent carbon atoms, and ultimately either a saturated or unsaturated substance :



Stress is laid on the view that the formation of the saturated and unsaturated substances is simultaneous and not successive, at least in the main. The constitution of the original carbonyl compound and the conditions of the reduction may determine which of the above four side reactions takes place preferentially, but the above mechanism is considered to be generally applicable.

Benzophenone, on reduction with zinc amalgam and aqueous hydrochloric acid, yields benzpinacone and traces of diphenylmethane; by reduction in alcoholic solution, tetraphenylethylene,  $\alpha$ - and  $\beta$ -benzpinacolin, and diphenylmethane may be obtained. Benzhydrol on reduction in alcoholic solution gives diphenylmethane, and the benzpinacolins give tetraphenylethylene.

Ethyl acetoacetate, on reduction in alcohol, gives ethyl crotonate and ethyl butyrate. Ethyl crotonate is not reduced to ethyl butyrate under similar conditions.

Ethyl laevulate yields ethyl valerate and an unsaturated ester, probably  $\beta$ -ethylidenepropionic ester.

Ethyl benzoylacetate on reduction in alcohol with amalgamated zinc yields  $\beta$ -diphenylpentadilactone (A., 1912, i, 889), ethyl  $\beta$ -phenylpropionate, and an oil, b. p.  $210-213^\circ/ < 1$  mm. Using amalgamated zinc, the products are the dilactone, ethyl cinnamate, ethyl  $\beta$ -phenylpropionate,  $\beta$ -diphenyl- $\Delta^2$ -crotonolactone- $\gamma$ -acetic acid, and probably *meso*- $\beta\beta'$ -dihydroxy- $\beta\beta'$ -diphenyladipic acid. Ethyl cinnamate on reduction with amalgamated zinc in alcoholic hydrogen chloride gives ethyl  $\beta$ -phenylpropionate.

Ethyl phenylglyoxylate gives ethyl mandelate and ethyl diphenyltartrate, and phenylglyoxylic acid yields mandelic acid.

Reduction of acetophenone in aqueous solution leads to ethyl benzene, acetophenonepinacolin, and styrene and its polymerisation products, along with small amounts of acetophenonepinacone, and  $\gamma$ -diphenylbutane (?). In alcoholic solution, the products are styrene and its polymerides, acetophenonepinacone and  $\alpha$ -chloroethylbenzene.

The products of reduction of benzaldehyde in aqueous solution are toluene, benzyl alcohol, stilbene, and hydrobenzoin. The action of zinc chloride on benzyl alcohol gives rise to stilbene hydrochloride.

C. K. I.

**The Isomeric Esters of Benzoylacrylic Acid.** GRACE POTTER RICE (*J. Amer. Chem. Soc.*, 1923, 45, 222—238).—The yellow methyl benzoylacrylate, obtained by Kozniewski and Marchlewski (cf. A., 1906, i, 759) can be converted into a colourless *stereo-isomeride*, m. p. 67°, by exposure to sunlight. The reverse change occurs if the colourless isomeride is exposed to sunlight in a solution containing a trace of iodine or bromine. Both the esters behave alike on oxidation by potassium permanganate in cold acetone solution, and they give the same product on treatment with nitromethane. Their behaviour towards alkaline reagents is not, however, the same. On boiling the yellow ester with dilute sodium carbonate solution, almost complete decomposition takes place, and it is not possible to isolate any benzoylacrylic acid. The colourless ester, under similar conditions, gives a 60% yield of benzoylacrylic acid. With concentrated hydrochloric acid, both the esters give a mixture of benzoylacrylic and  $\alpha$ -hydroxybenzoylpropionic acids. The benzoylacrylic acid obtained in either of these cases corresponds, in configuration, with the yellow ester.

The colourless ester reacts with two molecules of semicarbazide hydrochloride to give the *semicarbazone* of methyl  $\alpha$ -semicarbazidobenzoylpropionate, m. p. 177—178°. If, however, only one molecule of semicarbazide is used then the product is methyl  $\alpha$ -semicarbazidobenzoylpropionate, m. p. 150—150.5°, which when treated in cold acid solution with sodium nitrite gives methyl nitroso- $\alpha$ -semicarbazidobenzoylpropionate, m. p. 125°. With one molecule of semicarbazide the yellow ester gives the same product as the colourless ester, but with two molecules it yields methyl  $\alpha$ -semicarbazido-3-phenylpyrazolone-4-acetate, m. p. 172°, which when decomposed by hydrochloric acid gives the methyl semicarbazidobenzoylpropionate described above.

Ethyl benzoylacrylate was obtained in a yellow form, b. p. 184—185°/25 mm., and in a colourless form, m. p. 54°. As in the case of the methyl esters, the following products were prepared: the *semicarbazone* of ethyl  $\alpha$ -semicarbazidobenzoylpropionate, m. p. 187°; ethyl  $\alpha$ -semicarbazidobenzoylpropionate, m. p. 151—152°; ethyl nitroso- $\alpha$ -semicarbazidobenzoylpropionate, m. p. 127°; ethyl  $\alpha$ -semicarbazido-3-phenylpyrazolone-4-acetate, m. p. 171°.

Benzoylacrylic acid reacts with semicarbazide, and gives the same products whether one or two molecules of the latter are used, namely, two isomeric *semicarbazones*, m. p. 205° and 225°, respectively, and a *hydrate* of the former, m. p. 190°. All three compounds react with bromine as unsaturated compounds and two atoms of bromine are added on to the molecule, and a compound, m. p. 171°, is obtained. W. G.

**Dyes derived from Diphenic Anhydride.** SIKHIBHUSHAN DUTT (T., 1923, 423, 225—228).

**The Action of Bromine on Methylcoumaric and Methylcoumarinic Acids.** EINAR BILLMANN and HAKON LUND (*Ann. Chim.*, 1922, [ix], 18, 263—282).—The addition of bromine in anhydrous solution to methylcoumaric and methylcoumarinic

acids apparently results in the formation of a single product (cf. Fittig and Ebert, A., 1883, 474; Werner, A., 1906, i, 180), but Perkin (T., 1881, 39, 420) and Stoermer and Friemel (A., 1911, i, 632) have obtained indications of two acids resulting. The last-named workers isolated an acid, m. p. 170°; the authors' work confirms the formation of this single compound, but they were unable to determine its constitution with certainty, although the substance is presumed to be  $\alpha\beta$ -dibromo- $\beta$ -methoxyphenylpropionic acid. This acid on treatment with powdered zinc was converted into methylcoumaric acid, whilst water readily effected its hydrolysis into  $\alpha$ -bromo- $\beta$ -hydroxy- $\beta$ -methoxyphenylpropionic acid, crystals, m. p. 134°, which yields on dehydration  $\alpha$ -bromo- $\beta$ -methoxyphenylacrylic acid, obtained directly from  $\alpha\beta$ -dibromo- $\beta$ -methoxyphenylpropionic acid by Perkin (*loc. cit.*). The hydrolysis by which the acid was obtained must not be effected at a high temperature, otherwise carbon dioxide is evolved with formation of *methoxybromostyrene*, a light yellow oil, b. p. 142—143°/14—16 mm., whilst hydrobromic acid in acetic acid solution reverses the hydrolysis. Treatment of the acid with zinc powder results in the formation of methylcoumaric acid. The last-named substance yields on bromination by means of solution of bromine in aqueous potassium bromide,  $\alpha\beta$ -5-tribromo- $\beta$ -methoxy-5-phenylpropionic acid, which was also obtained from  $\alpha\beta$ -dibromo- $\beta$ -methoxyphenylpropionic acid and bromine water, and also by the action of hydrobromic acid on  $\alpha$ -5-dibromo- $\beta$ -hydroxy- $\beta$ -methoxyphenylpropionic acid. The latter was prepared by the action of bromine water on  $\alpha$ -bromo- $\beta$ -hydroxy- $\beta$ -methoxyphenylpropionic acid and forms crystals, m. p. 137°, isomeric with and transformed by heating into an acid of m. p. 155° identical with that prepared by Read and Andrews (T., 1921, 119, 1782). This acid may also be obtained by hydrolysis of  $\alpha\beta$ -5-tribromo- $\beta$ -methoxyphenylpropionic acid, the reaction being reversed by hydrobromic acid. Mercuric acetate and methylcoumarinic acid combine to form a mercuric compound (cf. A., 1900, i, 431). This was not isolated, but was used as an intermediate in the preparation of  $\beta$ -hydroxy- $\beta$ -methoxyphenylpropionic acid, which resulted from the elimination of the mercury by means of hydrogen sulphide. This acid has m. p. 88.5° and is quantitatively converted into methylcoumaric acid when boiled with dilute sulphuric acid, whilst bromine water yields a ring-substituted derivative, 5-bromo- $\beta$ -hydroxy- $\beta$ -methoxyphenylpropionic acid, m. p. 108°. All the ring-substituted bromo-compounds dealt with are converted on oxidation with permanganate into 2-methoxy-5-bromobenzoic acid, and the same substance was obtained by oxidation of methylcoumaric acid with permanganate and subsequent treatment of the methoxybenzoic acid so formed with bromine water.

H. J. E.

The Chemistry of the Glutaconic Acids. XIV. Three-carbon Tautomerism in the *cycloPropane* Series. FRANK ROBERT GOSS, CHRISTOPHER KELK INGOID, and JOCELYN FIELD THORPE (T., 1923, 123, 327—361).

**The Thermal Decomposition of certain Hydroaromatic Dicarboxylic Acids.** A. WINDAUS, W. HÜCKEL, and G. REVERBY (*Ber.*, 1923, 56, [B], 91—98).—Blanc's rule (A., 1907, i, 710), according to which pimelic and adipic acids are converted into cyclic ketones when heated at about 300° (in the presence of acetic anhydride if necessary), whereas glutaric and succinic acids give internal anhydrides under similar conditions, appears to be generally applicable in the aliphatic series. An experimental examination of the possibility of applying it in the hydroaromatic series has been undertaken, and the behaviour of certain hydroaromatic *o*-dicarboxylic acids is now described.

*cis*-cyclo-Hexane-1:2-dicarboxylic anhydride is decomposed at 380° into carbon dioxide, water, anthraquinone, and various hydrogenated derivatives of anthracene; its behaviour is thus similar to that of calcium succinate.

Homophthalic [*o*-carboxyphenylacetic] acid is smoothly hydrogenated in glacial acetic acid solution in the presence of platinum black to a mixture of *cis*- and *trans*-*o*-carboxycyclohexanecarboxylic acids from which the pure *cis*-acid is isolated by fractional crystallisation; it forms aggregates of prisms, m. p. 146°, and is converted by acetic anhydride into the corresponding *anhydride*, rectangular plates, m. p. 57°. The *cis*-acid is isomerised by hydrochloric acid at 200° to the *trans*-acid, colourless crystals, m. p. 157° (*anhydride*, short needles, m. p. 80—81°). When either *anhydride* is heated for a considerable time at 220°, an equilibrium mixture containing about 25% of the *cis*- and 75% of the *trans*-variety is produced.

*o*-Carboxyphenylpropionic acid is catalytically hydrogenated to *cis*-*o*-carboxycyclohexanepropionic acid, prisms, m. p. 103°; the calcium salt and the *di-anilide*, lustrous leaflets, m. p. 159°, are described. The acid is isomerised by concentrated hydrochloric acid at 180° to *trans*-*o*-carboxycyclohexanepropionic acid, prisms, m. p. 143°. The corresponding *di-anilide*, m. p. 212°, is prepared from the acid and aniline or by heating the *cis*-*di-anilide* at 250°; it can be distilled unchanged in a high vacuum. The *cis*- or the *trans*-acid is not converted into an alicyclic ketone containing one less atom of carbon when heated alone, but either acid is transformed by distillation with acetic anhydride into *hexahydro- $\alpha$ -hydrindone*,  $C_8H_{10} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CH}_2$ , a colourless liquid, b. p. 216°/758 mm.,  $d_4^{20}$  0.9982,  $n_D^{20}$  1.47915,  $n_D^{25}$  1.48117,  $n_D^{30}$  1.48827,  $n_D^{35}$  1.49342. The corresponding *semicarbazone* crystallises in needles, m. p. 214—215° (decomp.) when rapidly heated; the *oxime*, lustrous needles, m. p. 79—80°, is described. H. W.

**Total Hydrogenation of Naphthalic [Naphthalene-1:8-dicarboxylic] Acid.** J. CASARES and J. RANEDO (*Anal. Fis. Quim.*, 1922, 20, 519—526).—Naphthalene-1:8-dicarboxylic acid was hydrogenated to the tetrahydro- and decahydro-acids by the action of hydrogen in the presence of platinum. Specially purified reagents were used, and repeated activations were necessary.

The decahydronaphthalene-1:8-dicarboxylic acid thus obtained has no definite melting point, and is probably a mixture of *cis*- and *trans*-isomerides. Hydrogenation was effected more easily and without activations by use of the methyl and ethyl esters of naphthalic acid. Methyl tetrahydronaphthalene-1:8-dicarboxylate thus obtained from methyl naphthalate forms crystals, m. p. 74°. Ethyl tetrahydronaphthalene-1:8-dicarboxylate forms crystals, m. p. 52°, and has b. p. 193°/17 mm. Methyl decahydronaphthalene-1:8-dicarboxylate forms crystals, m. p. 103—105°. G. W. R.

**The Preparation of Benzenepentacarboxylic Acid.** KARL FLEISCHER and EWALD RETZE (*Ber.*, 1923, 56, [B], 228—234).—A new method of preparing benzenepentacarboxylic acid (cf. Fleischer and Siefert, A., 1920, i, 621), which starts from tetrahydronaphthalene, is described.

2-Ethyl-5:6:7:8-tetrahydronaphthalene condenses with diethyl-malonyl chloride in the presence of aluminium chloride and carbon disulphide to yield 2:2:4-triethyltetrahydronaphth- $\alpha\beta$ -indane-1:3-dione (annexed formula), colourless crystals, m. p. 39°. The substance is oxidised by nitric acid at 125—150° to 2:2-dicthyliindane-1:3-dione-4:5:7-tricarboxylic acid, colourless crystals, m. p. 249° (decomp.) after slight previous softening; when more drastically treated with nitric acid, it gives benzenepentacarboxylic acid, m. p. 232—233°.

2:2:4-Triethyltetrahydronaphth- $\alpha\beta$ -hydrindene, a colourless liquid, b. p. 203—205°/19 mm.,  $d_4^{20}$  0.9673,  $n_D^{20}$  1.5352, is isolated from the products of the action of amalgamated zinc and hydrochloric acid on 2:2:4-triethyltetrahydronaphth- $\alpha\beta$ -indane-1:3-dione. It condenses with acetyl chloride in the presence of aluminium chloride and carbon disulphide to yield 5-acetyl-2:2:4-triethyltetrahydronaphth- $\alpha\beta$ -hydrindene, colourless needles, m. p. 66° after softening at 63°, which, with *p*-nitrobenzaldehyde and potassium hydroxide solution, gives the corresponding *p*-nitrobenzylidene derivative,  $C_{28}H_{35}O_3N$ , canary-yellow needles, m. p. 161.5°. The acetyl compound is reduced by zinc and hydrochloric acid to 2:2:4:5-tetraethyltetrahydronaphth- $\alpha\beta$ -hydrindene, a pale yellow, very viscous liquid, b. p. 220—222°/20 mm.,  $d_4^{27}$  0.9647,  $n_D^{27}$  1.5365.

H. W.

**Dicyclic and Polycyclic Compounds with Bridged Linking.**  
*dicyclo*-[1,3,3]-Nonane and its Derivatives. HANS MEERWEIN [with FRANZ KIEL, GUSTAV KLÖSGEN, and EDWIN SCHOCH] (*J. pr. Chem.*, 1922, [ii], 104, 161—206; cf. A., 1913, i, 869).—*dicyclo*-[1,3,3]-Nonan-2:6-dione, the preparation of which has now been slightly improved, has been further characterised by the formation of the unsaturated diacetyl derivative of the dienol form, colourless needles, m. p. 78—79°. When the *disemicarbazone*, a white, crystalline powder, m. p. 226°, is heated for six hours at 230° with 10% ethyl-alcoholic sodium ethoxide solution (cf. Wolff,

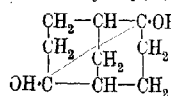
A., 1912, i, 988), dicyclononane (annexed formula), snow-white, feathery, plastic crystals, m. p. 145–146°, b. p. 168.5–170°, may be isolated from the product in 40% yield by distillation in steam. Reduction of the dicyclononandione with sodium amalgam gives a mixture of a tri-cyclononandiol (see below) and trans-dicyclo-

[1,3,3]-nonan-2:6-diol, m. p. 219°, which gives a reddish-violet coloration with alcohol and sulphuric acid, and a sapphire-blue coloration with acetic anhydride and sulphuric acid. The diacetate, m. p. 35°, b. p. 173–174°/17 mm., and the dibenzoate, glistening, white leaflets, m. p. 96–97°, are described. On oxidation with chromic acid, the dicyclo-glycol is reconverted into the diketone. When dehydrated with sulphuric acid, it gives dicyclo-[1,3,3]- $\Delta^6$ -nonen-2-ol, m. p. 133°, b. p. 224–226°, which has an intense camphor-like odour, is plastic, gives the same colour reactions as the dicyclo-glycol, and forms a liquid acetate, b. p. 111–112°/12 mm., having an intense odour resembling that of pine needles. This unsaturated alcohol, when reduced by means of hydrogen and platinum black, gives an 88% yield of dicyclo-[1,3,3]-nonan-2-ol, colourless crystals, m. p. 185°, which forms a liquid acetate, b. p. 128°/20 mm., and is oxidised by chromic acid mixture to dicyclo-[1,3,3]-nonan-2-one, plastic, colourless crystals, m. p. 150°; the ketone is characterised by the semicarbazone, colourless, needle-shaped crystals, m. p. 180–181°, the benzylidene derivative, m. p. 127–128°, which dissolves in concentrated sulphuric acid with a lemon-yellow coloration, and the cinnamylidene derivative, yellow needles, m. p. 116–117°, which similarly gives an orange-red coloration. Attempts to eliminate two molecules of water from the dicyclo-glycol have led only to resinous products, probably because the second double bond appears in the 5:6, and not the 6:7, position, the resulting hydrocarbon then isomerising to cyclooctatetrene, which is well known to polymerise easily.

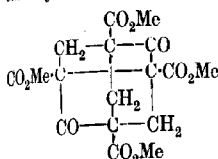
As mentioned above, the reduction of the dicyclo-diketone leads also to tricyclo-[1,3<sup>2</sup>,3<sup>2</sup>,0]-nonan-2:6-diol (annexed formula), which

may most readily be obtained by using the crude reduction product for the preparation of the dicyclononanol, it being then isolated from the sulphuric acid residue after the unsaturated alcohol has been removed in a current of steam. It forms glistening needles, m. p. 141°, is appreciably volatile in steam, dissolves without any coloration in concentrated sulphuric acid, and is oxidised by chromic acid in glacial acetic acid solution to the original dicyclo-diketone. The diacetate, tabular crystals, m. p. 121°, the dibenzoate, needles, m. p. 153–154°, and the diphenylurethane, fine needles, m. p. 201°, are described.

Methyl dicyclo-[1,3,3]-nonan-2:6-dione.1:3:5:7-tetracarboxylate forms with sodium methoxide (1 mol.) a white, crystalline monosodium derivative, which is decomposed by water into the free ester (1 mol.) and the disodium derivative (1 mol.); the latter, which

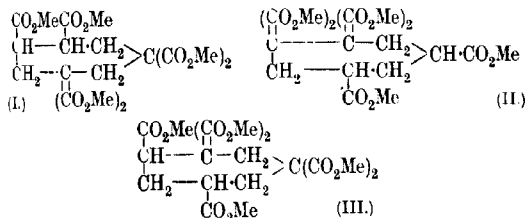


is directly produced from the ester and sodium methoxide (2 mols.), is a colourless, crystalline, hygroscopic powder, dissolving in water with opalescence. The action of bromine (2 atoms) on the monosodium derivative gives *methyl 3-bromodicyclo-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate*, rhombohedra, m. p. 154°, which is soluble in dilute alkalis and gives a reddish-violet coloration with ferric chloride. *Methyl 3:7-dibromodicyclo-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate*, colourless prisms, which is formed from the above-mentioned disodium derivative and bromine (5 atoms), is insoluble in alkalis, does not give a coloration with ferric chloride, and melts at 142° with elimination of bromine, giving *methyl tricyclo-[1,3,3',0]-nonan-2:6-dione-1:3:5:7-tetracarboxylate* (annexed formula), colourless prisms from xylene and



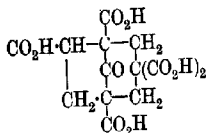
glacial acetic acid, leaflets from amyl-alcohol, m. p. 247—248°. The same compound is produced by the action of sodium and zinc dust in xylene solution on the dibromo-ester, by the action of bromine on the disodium derivative, or by the thermal decomposition of the *copper* compound of

the *dicyclo-tetracarboxylic* ester (A., 1913, i, 869), but is most readily prepared by treating the monobromo-ester with sodium methoxide (1 mol.), care being taken to avoid excess of alkali during the reaction. The tricyclic ester undergoes fission with methyl-alcoholic sodium methoxide, two molecules of methyl alcohol being taken up, with formation of a *methyl cycloheptanhexacarboxylate*, white needles from amyl alcohol, large prisms from methyl or ethyl alcohol, m. p. 128°, which must have one of the formulæ (I), (II), or (III), according as fission occurs in the positions 2:3 and 6:7, 1:2



and 5:6, or 1:2 and 6:7, respectively. The corresponding *cycloheptanhexacarboxylic acid*, obtained by hydrolysing the ester with aqueous barium hydroxide, separates from glacial acetic acid or anhydrous formic acid as a microcrystalline powder, m. p. 177° (decomp.), and loses carbon dioxide when heated with water and a trace of hydrochloric acid, giving *cycloheptane-1:3:5:6-tetracarboxylic acid*, m. p. 233°, which is probably a mixture of several of the five possible stereoisomeric forms, and may be derived equally well from any of the three possible hexacarbomethoxy-esters. Alternate formulæ are suggested for the *dianhydride*, m. p.

197—198°. When the *tricyclo*-ester is heated with aqueous barium hydroxide, hydrolytic fission of the bond 2 : 3(?) occurs, with formation of dicyclo-[1,2,3]-*octan-8-one-pentacarboxylic acid* (probable formula annexed), beautiful transparent prisms, which melt at 184—185° with evolution of carbon dioxide, but not of water.



Oxidation of the *dicyclononenol* (above) with chromic anhydride in glacial acetic acid solution gives dicyclo-[1,3,3]- $\Delta^6$ -*nonen-2-one*, a white, plastic mass, of camphor-like odour, m. p. 82°, b. p. 213—217°; it forms a *semicarbazone*, star-shaped clusters of needles, m. p. 190.5—191°, and a *cinnamylidene* derivative, yellow needles, m. p. 117°, which dissolves in concentrated sulphuric acid with an orange-red coloration. By the reduction of the dioxime of the *dicyclononandione* (A., 1913, i, 869) by means of sodium and *dicyclononandione* is produced as a alcohol, *trans-2 : 6-diaminodicyclo-[1,3,3]-nonane* is produced as a transparent, crystalline, hygroscopic mass, b. p. 125—130/14 mm., which has a strong odour characteristic of bases and rapidly liquefies in contact with the air. The dihydrochloride, colourless, non-hygroscopic, crystalline powder, the *diacetyl* derivative, glistening clusters of needles, m. p. 214°, and the *dibenzoyl* derivative, indefinite crystals, m. p. 351°, are described. Distillation of the dihydrochloride gives 2-aminodicyclo-[1,3,3]- $\Delta^6$ -*nonene*, a colourless, translucent, crystalline mass, m. p. 37.5°, b. p. 104°/17 mm., which rapidly liquefies on exposure to the air, possesses a strong odour reminiscent of both conine and nicotine, and is immediately oxidised by potassium permanganate in sulphuric acid solution.

Space formulae are used to indicate the absence of strain, not only in dicyclo-[1,3,3]-*nonane* itself, but also in the *tricyclopinacene*, the 2 : 6 bridge-bond of which is opened and closed with extraordinary ease, and in the *tricyclo-tetracarboxylic ester*, the production of which by the thermal elimination of free bromine provides an entirely new type of ring formation. Since the *dicyclononandionetetracarboxylic ester* is nearly "spannungslos," the ready formation by the action of sodium methoxide of a *cycloheptane* ring is taken to indicate that the latter is also free from strain, and therefore probably lies in more than one plane.

The stability of the *dicyclononandionetetracarboxylic ester*, and the ready fission of the *tricyclo*-ester, with alkaline reagents, are ascribed to the presence in the former, but not in the latter, of hydrogen attached to the ring-atoms 3 and 7 (cf. Dieckmann, A., 1901, i, 539).

A similarity is indicated between the physical properties of the *dicyclononane* derivatives and compounds of the camphor series; this does not, however, extend to the physiological properties, examples of which, contributed by Schüller, are quoted.

W. S. N.

**Cryoscopic Investigations on the Capacity to form Schiff's Bases.** BERNARDO ODDO and FRANCESCO TOGNACCHINI (*Gazzetta*, 1922, 52, ii, 347—361).—The method previously used (A., 1913, i,

1233; 1915, ii, 414, 415, and this vol., i, 255) has now been applied to the investigation of the course of the reaction between aniline and a number of aliphatic and aromatic aldehydes and ketones. The molecular weight, calculated from the depression of the freezing point of the aniline, is expressed as a percentage of the theoretical value for the aldehyde or ketone taken, and the result plotted as a function of the time.

Like all aromatic aldehydes, *p*-tolualdehyde reacts promptly with aniline, whereas phenylacetaldehyde reacts decidedly more slowly; with cinnamaldehyde, the reaction takes place more easily. As in the reaction with phenylhydrazine, anisaldehyde reacts with aniline far more rapidly than does vanillin, the hydroxyl group apparently exerting a retarding effect; a similar effect is exercised by a nitro-group in the meta-position to the aldehyde group. Anisaldehyde, cuminaldehyde, *p*-nitrobenzaldehyde, and *p*-tolualdehyde, all of which are substituted in the para-position, exhibit similar molecular weight-time curves.

The reaction is relatively slow with aromatic, and more rapid with aliphatic, ketones, mixed ketones showing intermediate behaviour. The results given by benzil, acetylacetone, and acetonylacetone show that the reactivity increases with the degree of separation of the two carbonyl groups; with benzil, however, it is doubtful if the reaction proceeds in the direction of the formation of the Schiff's base. Further, it seems that only one carbonyl group reacts in the case of  $\beta$ -diketones, whereas both carbonyl groups of the  $\gamma$ -diketones react. With acetylacetone and acetonylacetone, the experimental conditions, and with the former also the results obtained, preclude the formation of heterocyclic nuclei.

Camphor reacts not at all with aniline, and menthone and carvone only slowly. As regards the cyclohexane ketones, the reaction is slowest with the ortho- and most rapid with the para-substituted compounds, cyclohexanone occupying an intermediate position. Phenanthraquinone and santonin react slowly and phenolphthalein instantaneously, the stage reached in ten minutes persisting unchanged for twenty-one hours.

T. H. P.

**Preparation of  $\alpha$ -Homopiperonal from Safrole by the Action of Ozone, and Synthesis of its Derived Perfumes. I.** SHŌCHIRŌ NAGAI (*J. Chem. Ind. Japan*, 1922, 25, 1409—1421; cf. S. Nagai, *ibid.*, 1922, 25, 631).—By passing about 36 litres per hour of air containing 2—3% of ozone into a glacial acetic acid (10—15 parts) solution of safrole (1 part) at the ordinary temperature, safrole ozonide is produced readily. The ozonide is, however, liable to decompose spontaneously even at the ordinary temperature when freed from the solvent, or when heated, and is also readily polymerised into resinous matter by the effect of heat, air, alkali, etc. If the ozonide is decomposed by adding gradually water and zinc powder to the acetic acid solution, a yield of about 60—65% of  $\alpha$ -homopiperonal is obtained, which is further purified by conversion into the additive product with sodium hydrogen sulphite.  $\alpha$ -Homopiperonal is a light yellow oil, b. p.

131—133°/8 mm.,  $d_4^{20}$  1.2654,  $n_D^{20}$  1.5547, and gives an *oxime*, white needles, m. p. 119°, *semicarbazone*, white crystals, m. p. 176—177°, and *phenylhydrazone*, light yellow crystals, m. p. 176°. K. K.

**Gallaldehyde.** KARL W. ROSENMUND (*Ber.*, 1923, 56, [B], 136).—In reply to the recent observations of Nierenstein (this vol., i, 91), the author maintains that the acidity of gallaldehyde is sufficiently great to prevent its isolation from sodium carbonate solution in the manner described by Nierenstein. H. W.

**A New Compound from Conifer Distillates.** KARL CEDERQUIST and BROR HOLMBERG (*Ber.*, 1923, 56, [B], 298—300).—The formation of a solid product,  $C_{12}H_{16}O$ , was observed in the condensers during the purification of wood spirit distilled without previous neutralisation from pyroligneous acid derived from a mixture of pine wood (80%) and spruce wood (20%). It forms colourless prisms, m. p. 69—70°, and is optically inactive. It appears to be either an aldehyde or a ketone, since it is convertible into a *semicarbazone*, flattened needles or thin prisms, m. p. 198—199°, and two *oximes*, long, flattened prisms, m. p. 110—113°, and hairs or needles, m. p. 85—86°. H. W.

**Action of Organomagnesium Compounds on Nitriles. Action of Magnesium Phenyl Bromine.** LOUIS BARY (*Bull. Soc. chim. Belg.*, 1922, 31, 397—410).—The action of magnesium phenyl bromide on nitriles has been studied to compare it with that of magnesium methyl and ethyl bromides (cf. Bruylants, *Bull. Acad. roy. Belg.*, 1922, [v], 8, 7; Baerts, A., 1922, i, 817). In general far higher yields of ketone are obtained than is the case with the magnesium methyl and ethyl bromides, none at all, for example, being formed when these react with acetonitrile, whereas magnesium phenyl bromide gives a yield of about 45% of ketone. In the case of the aliphatic nitriles, the yield of ketone increases with increase of the length of the carbon chain.

In the case of benzonitrile, the intermediate product, diphenylketimine,  $CPh_2NH$ , was isolated in 75% yield, and is characterised by exceptional stability compared with those ketimines in which an alkyl group is united to the ketonic carbon. This is attributed to the fact that in diphenylketimine there is no possibility of tautomeric change of the type  $NH:CR:CH_2Me \rightleftharpoons NH_2:CR:CHMe$ . The nitrile of cyclopropanecarboxylic acid also gave a good yield of phenylcyclopropylketimine, a liquid of pungent, disagreeable odour, b. p. 135—136°/25 mm.,  $d_4^{20}$  1.0663,  $n_D^{20}$  1.56201. It is rapidly converted by dilute acid into phenyl cyclopropyl ketone (Perkin, T., 1885, 47, 840), a liquid of pleasant odour, b. p. 239°,  $d_4^{20}$  1.0566,  $n_D^{20}$  1.5565. The *semicarbazone* has m. p. 189°.

Phenylacetonitrile, acetonitrile, propionitrile, and *n*-butyronitrile yielded the ketone and condensation products, but the ketimine was not obtained. P. M.

**The Formation of Ketazines, Phenylhydrazones, and Semicarbazones of Ring-substituted Acetophenones.** W. J. BRUNING (*Rec. trav. chim.*, 1922, 41, [ii], 655—686).—In order to

ascertain whether acetophenone derivatives react with hydrazine, phenylhydrazine, and semicarbazide in an analogous manner to those of benzaldehyde, the author has studied the formation of ketazines, phenylhydrazones, and semicarbazones of ring-substituted acetophenones. The general conclusions drawn are (1) that glacial acetic acid is a suitable solvent for the preparation of such phenylhydrazones, (2) that the ketazines are only formed in acid solution, their preparation presenting no difficulty when hydrazine sulphate is used, whilst a boiling solution of hydrazine brings about no reaction, (3) that the nature of the ketone used is related to the speed of formation of the ketazine and conditions the state of equilibrium when formation and decomposition of ketazine are taking place at equal rates, (4) that the formation of the semicarbazones occurs more rapidly in acid than in alkaline or neutral solution, but excess of acid decomposes the semicarbazones into their constituents, and (5) that in some cases the nitro-group in the ortho-position with respect to carbonyl considerably diminishes the reactivity of the carbonyl group. The following substances are described: *p*-acetamidoacetophenoneketazine, yellow crystals, m. p.  $311^{\circ}$ ; *p*-acetamidoacetophenonephenylhydrazine, m. p.  $196-200^{\circ}$ ; *p*-acetamidoacetophenonesemicarbazone, white crystals, decomp.  $220^{\circ}$ ; 3:5-dibromo-*p*-aminoacetophenoneketazine, yellow crystals, decomp.  $297^{\circ}$ ; 3:5-dibromo-*p*-aminoacetophenonesemicarbazone, white crystals, m. p.  $255^{\circ}$  (decomp.); 3:5-dibromo-*p*-acetamidoacetophenone, m. p.  $188-189^{\circ}$ , yielding a ketazine, yellow, m. p.  $344^{\circ}$  (decomp.), a phenylhydrazone, pale yellow crystals, m. p.  $244-246^{\circ}$ , and a semicarbazone, white crystals, decomp.  $325^{\circ}$ ; 3:5-dibromo-*p*-diacetamidoacetophenone, obtained in two modifications, (a) unstable, m. p.  $67^{\circ}$ , which passes after some days into (b) stable, m. p.  $88^{\circ}$ ; 3:5-dibromoacetophenoneketazine, m. p.  $231^{\circ}$ ; 3:5-dibromoacetophenonephenylhydrazine, light yellow needles, m. p.  $109-110^{\circ}$ ; 3:5-dibromoacetophenonesemicarbazone, white crystals, m. p.  $134-135^{\circ}$ , yielding a ketazine, small, yellow crystals, m. p.  $300^{\circ}$ , a phenylhydrazone, yellow crystals, m. p.  $129-134^{\circ}$ , and a semicarbazone, white crystals, decomp.  $265^{\circ}$ ; 3:5-dibromo-2-nitroacetophenone, pale yellow crystals, m. p.  $133-144^{\circ}$ , yielding a ketazine, m. p.  $210^{\circ}$ , a phenylhydrazone, m. p.  $165-166^{\circ}$ , and a semicarbazone, m. p.  $234^{\circ}$  (decomp.); 3:4:5-tribromo-2-nitroacetophenone, white needles, m. p.  $188-189.5^{\circ}$ , yielding a ketazine, yellow needles, m. p.  $244^{\circ}$ , a phenylhydrazone, red crystals, m. p.  $173-174^{\circ}$ , and a semicarbazone, decomp.  $249^{\circ}$ .

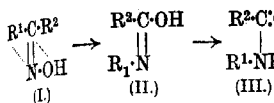
H. J. E.

The Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. VII. The Action of an Alcoholic Solution of Potassium Hydroxide on *p*-Hydroxy- and *p*-Ethoxybenzophenone and their *m*-Bromo-derivatives. P. J. MONTAGNE (*Rec. trav. chim.*, 1922, 41, 703-721; cf. A., 1920, i, 394).—The action of alcoholic potassium hydroxide on benzophenones effects the reduction of the carbonyl group to an alcoholic

group and also, in the case of halogen-substituted benzophenones, the partial replacement of halogen atoms in the ring by hydrogen. A retarding action is exerted by the ethoxyl group in the para-position; this is considerably diminished by the presence of a bromine atom in a similar position in the other ring. In the case of benzophenone itself, heating at  $100^{\circ}$  for two days completes the reduction, whilst on heating 4-ethoxybenzophenone for six days under similar conditions so little change occurs that it is found impossible to isolate the reduction product. On introducing a bromine atom into the meta-position in the ring to which the ethoxyl group is attached, the greater part of the substance is reduced after two days; a second bromine atom in the meta-position in the same ring entirely masks the retarding effect of the ethoxyl group and the substance behaves similarly to benzophenone. The author points out that the action of bromine is similar in the case of 4:4'-dibromo-3:3'-diaminobenzophenone (A., 1917, i, 143). None of the corresponding hydroxybromobenzophenones is reduced even after prolonged heating, so that the effect of the hydroxyl group in inhibiting reduction is not diminished to any appreciable extent by bromine. The products resulting from the action of alcoholic potassium hydroxide on 3:5-dibromo-4-ethoxybenzophenone are 3:5-dibromo-4-ethoxybenzhydrol, 3-bromo-4-ethoxybenzhydrol, and 3:5-dibromo-4-hydroxybenzophenone, the two last-named being formed in small quantity. Hydrolysis of the ethoxyl group thus takes place to a limited extent. The introduction of a second ethoxy-group into the other ring increases the influence of the first and reduction is then incomplete after heating for six days.

The following substances were prepared: 3'-bromo-4-hydroxybenzophenone, crystals, m. p.  $171^{\circ}$ ; 3-bromo-4-ethoxybenzophenone, rhombic bipyramidal crystals ( $a:b:c=0.7935:1:0.2691$ ), m. p.  $102.25^{\circ}$ ; 3-bromo-4-ethoxybenzhydrol, colourless crystals, m. p.  $85^{\circ}$ ; 3:5-dibromo-4-ethoxybenzophenone, colourless, monoclinic crystals ( $a:b:c=1.0901:1:0.8591$ ;  $\beta=59^{\circ}41'$ ), m. p.  $83.5^{\circ}$ , b. p.  $244^{\circ}/11$  mm.; 3:5-dibromo-4-ethoxybenzhydrol, small needles, m. p.  $81.75^{\circ}$ ; 3'-bromo-4-ethoxybenzophenone, colourless crystals, m. p.  $79.5^{\circ}$ , b. p.  $232^{\circ}/11$  mm.; 3-bromo-4-ethoxybenzhydrol, needles, m. p.  $43^{\circ}$ ; 3:5-dibromobenzophenone, m. p.  $75^{\circ}$ , b. p.  $232^{\circ}/18$  mm.; 4:4'-diethoxybenzophenone, small, colourless plates, m. p.  $132^{\circ}$ , b. p.  $258^{\circ}/15$  mm.; 4:4'-diethoxybenzhydrol, crystals, m. p.  $50^{\circ}$ . 4-Ethoxybenzophenone crystallises in the monoclinic system ( $a:b:c=0.7427:1:1.6049$ ;  $\beta=87^{\circ}58'$ ). H. J. E.

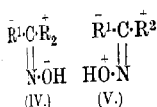
**Formation and Transformation of the Naphthyl Ketoximes.** ERNST BECKMANN, OTTO LIESCHE, and ERICH CORRENS (*Ber.*, 1923, 56, [B], 34<sup>1</sup>—354).—The isomerism of ketoximes has been explained by Hantzsch and Werner in accordance with the principles of ethylenic isomerism and the arbitrary but plausible assumption that the vicinal groups in these compounds exchange places during the course of the Beckmann transformation has been generally accepted until recently. Bucherer, however (*Lehrbuch der Farbenchemie*, 1914), has put forward a scheme in which the



subsidiary valencies (I) are considered to become converted under the conditions of the change into principal valencies with consequent

conversion of the form I into form II, from which the stable modification (III) of the transformation product is readily derived. The transformation thus consists in a change of position between the hydroxyl group and the oppositely situated radicle. Similar views have been expressed more recently by Biltz and Robl (A., 1921, i, 891) and by Meisenheimer (A., 1922, i, 152, 176). The conception has the advantage that the chemical unity of the molecule is regarded as being in a measure preserved throughout the change whereas the direct exchange of position of two neighbouring groups is scarcely possible without intermediate rupture of the molecule.

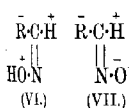
Confirmation of this view of the transformation is deduced in a somewhat different manner. In accordance with Abegg's electrochemical view of the stability of oximes, the disposition of the relatively positive and negative radicles in the alkali-stable and "acid-stable" oximes must be that shown in the annexed formulæ (IV) and (V). It is found that in the "alkali-stable" form the



more strongly negative radicle, R<sup>1</sup>, wanders, whereas in the "acid-stable" variety the less strongly negative radicle, R<sup>2</sup>, migrates during the Beckmann change. The evidence is based on the behaviour of the phenyl naphthyl ketoximes (Betti and Becciolini,

A., 1916, i, 49; Poccianti, A., 1915, i, 822) and the dinaphthyl ketoximes in which, in accordance with the dissociation constants of the corresponding carboxylic acids, the phenyl and β-naphthyl groups are considered to be about equally negative and considerably inferior in this respect to the α-naphthyl radicle.

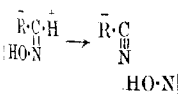
Difficulties appear to be encountered when these views are applied to aldioximes. The varieties which readily yield nitriles



are in general favoured by the action of acids and to them the constitution VI must be ascribed, whereas the isomerides which can be successively esterified and hydrolysed without undergoing decomposition must have the configuration, VII. This, however, is

contrary to the accepted view that the water-forming groups must be obtained from vicinal positions in the compound. The

change is possibly explicable in accordance with the annexed scheme. In any case it appears to be established that in the acid-stable variety of aldioximes (*syn*-oxime) the hydrogen, as positive radicle, wanders when the change results



in the formation of a nitrile or when a normal Beckmann rearrangement occurs.

*Di-β-naphthylketoxime*, needles, m. p. 180—181°, is converted by phosphorus pentachloride in the presence of anhydrous ethyl ether into *β-naphtho-β-naphthylamide*, colourless, lustrous needles, m. p. 239°, the constitution of which is established by its synthesis from *β-naphthoyl chloride* and *β-naphthylamine*. *Di-α-naphthylketoxime*, small, colourless needles, m. p. 200°, is transformed similarly into *α-naphtho-α-naphthylamide*, m. p. 241°. *α-Naphthyl-β-naphthyl ketone*, m. p. 135°, is prepared by the action of magnesium *α-naphthyl bromide* on *β-naphthonitrile* (the intermediate compound,  $\alpha\beta\text{-(C}_{10}\text{H}_7)_2\text{C:N-MgBr}$ , yellow crystals, m. p. 255°, was isolated); it is converted quantitatively in acid solution at 135—140° into *α-naphthyl β-naphthyl ketoxime*, m. p. 171°, which is transformed into *α-naphtho-β-naphthylamide*, colourless needles, m. p. 200°, identical with the product obtained by the action of *α-naphthoyl chloride* on *β-naphthylamine*. H. W.

**Studies in the Anthracene Series. IV.** EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS (T., 1922, 123, 380—394).

**Benzaurin.** RICHARD MEYER and WILLY GERLOFF (*Ber.*, 1923, 56, [B], 98—104).—In a previous communication (Meyer and Fischer, A., 1913, ii, 167) it has been shown that the absorption spectrum of benzaurin is so similar to that of fuchsone that it must almost necessarily be regarded as a *p*-hydroxyfuchsone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ . Analysis of the dye, however, gives results which are in harmony with the formula  $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{OH})_2$ . It is found, however, that a molecular proportion of water is readily lost when the dye is heated, and that the residue has the composition of *p*-hydroxyfuchsone. Benzaurin is therefore regarded as a hydrate of *p*-hydroxyfuchsone. This conception explains the behaviour of the substance when dissolved in alcohol or acetic acid (Meyer and Fischer, *loc. cit.*), the deepening in colour observed when the alcoholic solution is warmed and the formation of an orange-coloured solution in the cold acid being attributable to the withdrawal of water and the production of the more intensely coloured *p*-hydroxyfuchsone.

Since benzaurin obtained by Doebner's method, from benzotrichloride and phenol (*p*-hydroxybenzophenone is formed as by-product) is not crystalline and has not a definite melting point, various attempts have been made to secure a more definitely homogeneous product. The oxidation of 4:4'-dihydroxytriphenylmethane, m. p. 161° (acetate, m. p. 115°), or the hydrolysis of benzaurin diacetate, m. p. 119°, or *benzaurin dibenzoate*, colourless needles, m. p. 183—184°, did not lead to the desired result. More success is obtained by decomposing benzaurin perchlorate (cf. Pfeiffer, A., 1917, i, 210) with the requisite quantity of sodium hydroxide and subsequently adding dilute sulphuric acid, whereby benzaurin is caused to separate as a brilliant red precipitate. It loses one molecular proportion of water at 110—120°.

*Benzaurin hydrochloride*, dark red needles, is obtained by the

addition of an excess of fuming hydrochloric acid to a solution of benzaurin in glacial acetic acid. H. W.

**Di- and Tri-hydroxydeoxybenzoins.** ERNEST CHAPMAN and HENRY STEPHEN (T., 1923, 123, 494-499).

**The Reactivity of Doubly-conjugated Unsaturated Ketones.**  
**IV. The Effect of Substitution on the Reactivity of 4'-Dimethylamino-2-hydroxydistyryl Ketone.** ISIDOR MORRIS HEILBRON and ABRAHAM BRUCE WHITWORTH (T., 1923, 123, 238-245).

**The Benzilic Acid Transformation.** I. G. SCHEUING (*Ber.*, 1923, 56, [B], 252-259).—It is shown that the bluish-violet dye which is produced during the preparation of benzilic acid from benzil and ethyl-alcoholic potash has no direct effect on the transformation. The attempts which have been made previously to explain the course of the benzilic acid transformation assume the rupture of one or both double bonds between the carbon and oxygen atoms of benzil by the addition of water or potassium hydroxide. Such compounds have now been isolated.

*Benzil potassium hydroxide*,  $C_{14}H_{10}O_2.KOH$ , small, indistinct, pale yellow crystals, is obtained when an intimate mixture of benzil and dry potassium hydroxide is triturated beneath a little pyridine or benzene, or by the addition of a concentrated alcoholic solution of potassium hydroxide to a cold solution of benzil in ether. It is decomposed into its components by water and into potassium hydrogen carbonate and benzil by dry carbon dioxide. It is converted slowly at 0°, in a few hours at the atmospheric temperature, and almost instantaneously at 80°, into potassium benzilate, so that it appears to be a definite intermediate product of the conversion of benzil into benzilic acid.

In a similar manner, the addition of a solution of potassium in methyl alcohol and ether to an ethereal solution of benzil leads to the separation of the compound  $C_{14}H_{10}O_2.MeOK.MeOH$ , small, almost colourless crystals, which is decomposed by water, alcohol, or carbon dioxide in the same manner as the product from potassium hydroxide. On the other hand, it does not undergo a similar smooth transformation, which only occurs to the extent of 15% when it is preserved beneath ether during two days at the atmospheric temperature. The product of the change is benzilic acid, whereas methyl benzilate or methoxydiphenylacetic acid would be expected. Transformation does not take place to any considerable extent when it is heated in the presence of benzene; the main products are unchanged benzil and benzoïn, the latter being formed owing to the reducing action of potassium methoxide. *Benzil sodium ethoxide*,  $C_{14}H_{10}O_2.EtONa$ , a pale yellow, distinctly crystalline substance, is prepared by the addition of sodium ethoxide dissolved in a mixture of ethyl alcohol and xylene to a solution of benzil in the latter solvent. The formation of benzil potassium ethoxide can only be observed at a low temperature; it becomes altered in an unexplained manner at 0°. H. W.

**The Beckmann Transformation in the Cases of *o*- and *p*-Quinoneoximes.** ERNST BECKMANN and OTTO LIESCHE (*Ber.*, 1923, 56, [B], 1—23).—The experiments described do not establish beyond all doubt the normal course of the Beckmann transformation in the cases of *p*- and *o*-quinones. The expected enlargement of the ring appears to be proved most conclusively in the instance of anthraquinonemonoxime. The direct action of the transforming agents on dioximes does not appear to lead to the production of an eight-membered ring containing two nitrogen atoms, but this seems possible in the case of anthraquinone if the monoxime is first transformed and the product converted into its oxime and again transformed.

I. *Phenanthraquinone- and naphthaquinone-oxime* [with HERBERT DIETRICH].—The action of phosphorus pentachloride on  $\beta$ -naphthaquinoneoxime [2-nitroso- $\alpha$ -naphthol] has been studied by Borsche and Sander (*A.*, 1915, i, 299), who have isolated a product to which they ascribe the constitution  $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CN}$ , but for which the cyclic structure,  $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{CCl}=\text{N} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}\text{CO}$ , appears to the authors to

be equally possible. The same chloride, colourless, matted needles, m. p.  $80^\circ$ , is obtained by the action of phosphorus pentachloride on the oxime in the presence of light petroleum. It is converted by ammonia in the presence of anhydrous ether into the substance  $\text{C}_{10}\text{H}_6\text{ON}_2$ , m. p.  $207^\circ$ , and by boiling water into the monobasic acid,  $\text{C}_{10}\text{H}_6\text{O}_2\text{N}$ , m. p.  $179^\circ$ , the *silver*, *sodium*, *potassium*, and *barium* salts of which are described. It is hydrolysed by boiling aqueous sodium hydroxide solution to *o*-carboxycinnamic acid, m. p.  $184^\circ$  (the *silver* salt is described). The action of a saturated solution of hydrogen chloride in a mixture of glacial acetic acid and acetic anhydride or of benzenesulphonyl chloride in the presence of pyridine on  $\beta$ -naphthaquinoneoxime gives the acid,  $\text{C}_{10}\text{H}_6\text{O}_2\text{N}$ , m. p.  $179^\circ$ , the properties of which appear to the authors to be compatible with either the cyclic or open structure.

$\beta$ -Naphthaquinonedioxime is converted by phosphorus pentachloride in the presence of light petroleum by the Beckmann mixture and by benzenesulphonyl chloride and pyridine into the anhydride,  $\text{C}_{10}\text{H}_6\text{ON}_2$ , m. p.  $81^\circ$ , the ready formation of which causes a stabilisation which inhibits the Beckmann transformation.

$\alpha$ -Naphthaquinonemonoxime [4-nitroso- $\alpha$ -naphthol] does not undergo a smooth transformation with any of the reagents investigated. With Beckmann's mixture, it yields a compound,  $\text{C}_{12}\text{H}_8\text{O}_3\text{NCl}_2$ , long needles, m. p.  $165^\circ$  after previous softening. With benzenesulphonyl chloride and pyridine, the *ester*,

$\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{C}(\text{O}\cdot\text{SO}_2\cdot\text{h})\cdot\text{CH} \\ \text{C}(\text{NO})=\text{CH} \end{smallmatrix}$ , colourless, matted needles, m. p.  $182$ —

$184^\circ$ , is produced.  $\alpha$ -Naphthaquinonemonoxime is not affected by boiling acetyl chloride, but is converted by the cold reagent into ill-defined compounds containing halogen. The *acetyl* derivative,

$\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{C}(\text{OAc})\cdot\text{CH} \\ \text{C}(\text{NO})=\text{CH} \end{smallmatrix}$ , lustrous, brown needles, m. p.  $132.5^\circ$ , is obtained readily by the action of acetic acid and acetic anhydride;

it does not yield homogeneous products when treated with the transforming agents.

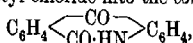
$\alpha$ -Naphthaquinonedioxime is converted by the Beckmann mixture into the corresponding diacetate, m. p. 164°, which is transformed by the reagent at a higher temperature into ill-defined chlorinated compounds.

II. *Benzoquinone- and Anthraquinone-oximes* [with A. PHILIPPICH VON PHILIPPSBERG].—*p*-Benzoquinonemonoxime is converted by benzenesulphonyl chloride in the presence of pyridine into the corresponding ester, m. p. 131°, which (without being isolated) is transformed by being further heated and subsequently treated with sulphuric acid into the compound,  $\text{CO} \begin{smallmatrix} \text{CH:CH}\cdot\text{CO} \\ \text{CH:CH}\cdot\text{NH} \end{smallmatrix}$ , yellowish-

brown needles, m. p. 224°. The substance dissolves in solutions of alkali hydroxides and carbonates yielding solutions from which the cobalt, silver, molybdenum, manganese, tin, zinc, lead, and iron salts are prepared; it gives a benzoyl derivative, leaflets, m. p. 189—190°.

Many attempts are described to effect the transformation of *p*-benzoquinonedioxime, but these have not been successful. Apparently the conversion only occurs if a certain minimum temperature is exceeded (below which only salt formation takes place). With the compound in question, this temperature is so high that, when augmented by the local and unavoidable heat of the reaction, it causes the extensive decomposition of the products of the change.

Anthraquinonemonoxime is converted by a mixture of phosphorus pentachloride and acetyl chloride into the compound,



short, colourless needles, m. p. 245°, which is transformed by successive treatment with boiling sodium hydroxide solution and acid into 2-*o*-aminobenzoylbenzoic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 199° (decomp.), the silver, lead, and copper salts of which are described. It yields a methyl ester, m. p. (indefinite) 168—173°. The presence of the amino-group is established by its ability to yield a diazo-compound. Anthraquinonemonoxime is converted by a mixture of phosphorus pentachloride and phosphoryl chloride into the phosphoric acid derivative, which is isolated as the silver salt,  $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C:N}\cdot\text{O}\cdot\text{PO}(\text{OAg})_2$ , whereas benzenesulphonyl chloride and pyridine transform it into the corresponding ester,  $\text{C}_6\text{H}_5\text{O}_2\text{NS}$ , slender, colourless needles, m. p. 154°. The transformation product,  $\text{C}_{14}\text{H}_9\text{O}_2\text{N}$ , is converted by further treatment with hydroxylamine hydrochloride in boiling alcoholic solution

(86%) into the corresponding oxime,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{NOH}) \\ \text{CO}\cdot\text{HN} \end{smallmatrix} \text{C}_6\text{H}_4$ , colourless needles, m. p. 243° (decomp.) [*benzoyl* derivative, m. p. 206°], which is converted by the Beckmann mixture at 170° into

phthalyl-*o*-phenylenediamine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p. 275—

278°, identical with the product synthesised by Anderlini and Meyer (A., 1906, i, 765), for which, however, an alternative constitution has been suggested by Thiele and Falk (A., 1906, i, 750).  
H. W.

**Arylamine Salts of the Anthraquinonesulphonic Acids.**  
A. G. PERKIN and W. G. SEWELL (*J. Soc. Chem. Ind.*, 1923, 42, 27—31†).—The arylamine salts of the anthraquinonesulphonic acids are well-defined crystalline substances, sparingly soluble in water or alcohol. They are readily obtained by adding an acid solution of the arylamine hydrochloride to a solution of the sodium salt of the sulphonic acid. The salts are useful for the purification of the alkali salts of the sulphonic acids, and they can also be used for transforming one alkali or alkaline-earth salt into another, as they are easily reconverted into a metallic salt by boiling with the requisite quantity of either aqueous or alcoholic alkali or alkaline-earth hydroxide. Certain of these salts, notably the aniline salts, can be employed with fair exactitude for the analysis of anthraquinone-mono- and -di-sulphonates by titrating a suspension of the aniline salt in boiling water with standard alkali hydroxide in presence of phenolphthalein. Advantage can be taken of the sparing solubility of the methylaniline, compared with the dimethylaniline  $\beta$ -sulphonates, to effect a fairly complete separation of methylaniline from a mixture of the two bases, provided it is present in considerable amount. The following are among the salts described: *Aniline anthraquinone-2-sulphonate*, colourless needles, m. p. 309°; *p-toluidine anthraquinone-2-sulphonate*, colourless needles, m. p. 308°;  *$\alpha$ -naphthylamine 2-sulphonate*, m. p. 253°; *aniline anthraquinone-1-sulphonate*, m. p. 284°; *methyl-aniline anthraquinone-2-sulphonate*, m. p. 202—203°; *dimethylaniline 2-sulphonate*, m. p. 192—194°; *1-sulphonate*, m. p. 215°; *diethyl-aniline anthraquinone-2-sulphonate*, m. p. 174—175°; the aniline salts of the following anthraquinonedisulphonic acids, 1:5-, orange-yellow crystals; 1:8-, needles; 2:6-, plates; and 2:7-, plates; none of these salts exhibited a melting point. The *methyl-aniline* salts of the 1:5-disulphonic acid, m. p. 251°, orange plates; 1:8-disulphonic acid, 2:6-disulphonic acid, needles, m. p. 205—210°, and 2:7-disulphonic acid, m. p. 230°, are described, as also are the corresponding dimethylaniline salts. *Quinoline anthraquinone-1-sulphonate* melts at 195°, and the *2-sulphonate* at 225°. *Pyridine anthraquinone-1-sulphonate* forms needles, m. p. 158°.  
G. F. M.

**The Camphor Series. II.** SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1922, 6, 55—72).—[With KITARO FUJII].—Applying Reformatzky's synthesis to *d*-camphor, using ethyl, *l*-menthyl, and *d*-bornyl esters of iodoacetic acid, esters of bornylacetic acid were obtained, all of which gave the same *l*-isobornylacetic acid on hydrolysis. *Ethyl isobornylacetate*,  $C_{15}H_{26}O_2$ ,  $C(OH)CH_2CO_2Et$ , is a viscous liquid, b. p. 108—112°/3 mm.,  $[\alpha]_D^{25} -24.97^\circ$ . *l*-Menthyl isobornylacetate was obtained as a syrup. *d*-Bornyl isobornylacetate, m. p. 196—197°, has  $[\alpha]_D^{25} +17.44^\circ$ . *l*-Bornylacetic acid,

prepared from the ethyl ester, had  $[\alpha]_D^{20}$   $-20.32^\circ$ , from the *d*-menthyl ester,  $-19.85^\circ$ , and from the *d*-bornyl ester,  $-25.62^\circ$ , all in alcohol. For the barium salt in water, values of  $[\alpha]_D^{20}$  from  $9.53^\circ$  to  $12.91^\circ$  were observed.

[With SHOZO YAMAGUCHI.]—When *d*-camphoroxime was reduced by Forster's method in amyl alcohol with sodium, *d*-bornylamine and *l*-isobornylamine were formed in the proportions of 65.9% of the former to 34.1% of the latter. The high proportion of laevo compound formed, compared with the proportion of *l*-borneol formed by the reduction of *d*-camphor, 19%, may be attributed to the influence of the more positive amino-group on the asymmetric transformation of the carbonyl carbon atom in the camphor molecule. When *d*-bornylamine was passed over thoria at  $400^\circ$ , it was decomposed into camphene and ammonia.

[With RISABURO NAKAI.]—When *d*-borneol was passed over thoria at  $400^\circ$  with ammonia gas, no bornylamine was formed, but *d*-camphene was obtained; in the same way, *l*-borneol gave *l*-camphene. It is probable that camphene was not formed directly from borneol by the Wagner rearrangement, but through the intermediate formation of bornylamine which, as shown above, decomposes into camphene and ammonia. Both *d*- and *l*-camphene gave the same *l*-isocamphene when reduced with hydrogen in presence of nickel. Some specimens of *d*-camphene were found to solidify on keeping; the crystals had m. p.  $50^\circ$ ,  $[\alpha]_D^{20} +17.61^\circ$ . The question of the existence of solid and liquid forms of camphene is being further investigated.

E. H. R.

**Pinene of Spanish Turpentine.** A. MADINAVEITIA (*Anal. Fis. Quim.*, 1922, 20, 531–533).—By fractional distillation of different samples of Spanish turpentine, collecting the fraction  $154.5$ – $157^\circ$ , yields of pinene varying from 35 to 90% are obtained. Except in the case of turpentine from *Pinus halepensis*, the pinene obtained is dextrorotatory. The differences in yield of pinene by fractional distillation are attributed to the presence of varying amounts of nopinene.

G. W. R.

**Castelamarin—A Bitter Principle from *Castela Nicholsoni*.** LOUIS PIERRE BOSMAN (*T.*, 1923, 123, 207–210).

**Chinese Tannin.** J. HERZIG (*Ber.*, 1923, 56, [B], 221–228).—The methylation of Chinese tannin by means of diazomethane has been reinvestigated and methylotannin (cf. Herzig and Tscherne, A., 1905, i, 254) has been prepared in excellent yield. As judged by the specific rotation and methoxyl content, the product must be regarded as homogeneous; if this is the case, the yields show that the parent substance of methylotannin must be present to the extent of at least about 90% in Chinese tannin. Additional evidence of the chemical individuality of Chinese tannin is thus adduced (cf. Iljin, A., 1914, i, 587; Freudenberg, A., 1922, i, 1170). The main reason for the poor yields of methylotannin which have been encountered frequently is to be found in ester transformation, which leads to the production of methyl trimethoxy-

benzoate. In two instances, methyl pentamethyl-*m*-digallate was isolated and this appears to be the first instance in which this compound has been prepared from Chinese tannin directly. The improvement in the methylation of the tannin is brought about by the preliminary, repeated distillation of the ethereal solution of the diazomethane at as low a temperature as possible, and with the help of a dephlegmator. The residue, after removal of the excess of the reagent and desiccation in a vacuum, is solid and can be powdered; occasionally it is obtained directly in pulverulent form. It is almost completely insoluble in cold methyl alcohol, after treatment with which it has a methoxyl content almost identical with that of methylotannin obtained previously. After further purification from warm methyl alcohol, it has  $[\alpha]_D^{25} + 12.44^\circ$ ,  $[\alpha]_D^{25} + 12.75^\circ$ ,  $[\alpha]_D^{25} + 12.22^\circ$  in benzene solution (2%), whereas Herzig and Renner (A., 1909, i, 713) found  $+9^\circ$  to  $+11^\circ$ .

H. W.

#### [Tannins and Similar Substances. II. Chinese Tannin.]

KARL FREUDENBERG and WILHELM SZILASI (*Ber.*, 1923, 56, [B], 406).—The preparation of highly active Chinese tannin (A., 1922, i, 1169) only succeeds when the crude tannin,  $[\alpha]_D^{25} + 90^\circ$ , has remained for a protracted period in aqueous solution in contact with aluminium hydroxide.

H. W.

**Reduction of an Indanthrene Dye by Means of Sodium Hyposulphite.** JOHN H. YOE and GRAHAM EDGAR (*J. Physical Chem.*, 1923, 27, 65—73).—The reaction between an oxyindanthrene dye (Ponsol-yellow-G) and sodium hyposulphite has been investigated, and it is shown that the reduction and solution of the dye involve (a) the comparatively rapid reaction of the dye with the hyposulphite to form an insoluble crystalline reduced dye, and (b) peptisation of the latter by hydroxyl-ions, with the formation of a colloidal solution. The rate of solution and the amount of dye peptised by a given solution depend on the state of subdivision of the dye. Positive ions tend to coagulate the solution and to retard the peptisation of the reduced dye.

J. S. G. T.

**Ability of Alkaloids to Form Oxides. Oxygenase of the Bach-Chodat System.** OBDULIO FERNÁNDEZ and ANTONIO PIZARROSO (*Anal. Fis. Quim.*, 1922, 20, 589—594; cf. Fernandez, A., 1921, i, 485).—The ability of a number of alkaloids and other compounds containing the group  $-\text{CO}-\text{NH}-$  to form oxides in the presence of hydrogen peroxide is investigated. The conclusions drawn are indefinite.

G. W. R.

**Aristolochic Acid.** ARMAND CASTILLE (*J. Pharm. Belg.*, 1922, 4, 569—571; from *Chem. Zentr.*, 1922, iii, 1301).—Aristolochic acid from *Aristolochia clematis*, *A. longa*, and *A. rotundifolia*, is identical with Pohl's aristolochine (A., 1892, 874). It has molecular weight 343 and corresponds with the formula  $\text{C}_{17}\text{H}_{11}\text{O}_4\text{N}$ . It gives on reduction a substance,  $\text{C}_{17}\text{H}_{13}\text{O}_4\text{N}$ , which is characterised by its fluorescence in solution, and probably contains an anthraquinone nucleus.

G. W. R.

**Aldehydes derived from Cinchonine, Quinine, and their Acyl Compounds.** L. SEEKLES (*Rec. trav. chim.*, 1923, 42, 39-104).—When quinine, cinchonine, or their acetyl or benzoyl derivatives are subjected to the action of ozone in cold chloroform solution, addition occurs at the double linking of the vinyl group with formation of an ozonide which, when treated with water, decomposes into formaldehyde and a new aldehyde. The terms quininal and cinchoninal are suggested for the new aldehydes from quinine and cinchonine, respectively. These and a large number of their derivatives are described. *m*-Chloropiperic acid (3-chloro-2:4:6-trinitrophenol) was found useful for obtaining derivatives of the new aldehydes, since it readily precipitated them in a crystalline form and an estimation of chlorine provided a ready method of analysis. The following new salts of this acid were prepared.

Quinine+2X (X=*m*-chloropiperic acid), yellow, m. p. 217° (decomp.); cinchonine+X, yellow, crystalline, clusters, m. p. 198°; +2X, greenish-yellow crystals, m. p. 209°; acetylcinchonine+X, greenish-yellow, m. p. 188°; +2X, yellow, m. p. 143-144°; benzoylcinchonine+X, yellow, m. p. 140-141°; +2X, yellow, m. p. 156°; acetylquinine+2X, m. p. 139°; benzoylquinine+X, greenish-yellow, m. p. 129-130°; +2X, yellow crystals, m. p. 150°.

Acetylcinchonine when pure has  $[\alpha]_D^{25} +139.5^\circ$  in water containing 3 mols. HCl; it could not be crystallised. Acetylquinine under the same conditions has  $[\alpha]_D^{25} -120.8^\circ$ , m. p. 116°. It crystallises in the bisphenoidal class of the rhombic system, *a*:*b*:*c*=1.1142:1:0.6119.

Acetylcinchonine ozonide forms a white, voluminous mass, softening at 75°, decomposing at 95-100°. Acetylcinchoninal was obtained as a white, amorphous substance having a marked tendency to polymerise, m. p. 106-109°;  $[\alpha]_D^{25} +28.2^\circ$ . Attempts to hydrolyse the acetyl group were unsuccessful. It forms a *mono-m-chloropiperic*ate, m. p. 155°, and a *di-m-chloropiperic*ate, m. p. 156-165°. The *phenylhydrazone* of acetylcinchoninal is an amorphous powder, m. p. 135-142°, *acetate*, amorphous, m. p. 106°; *p-bromophenylhydrazone*, yellow powder, m. p. 126°, *acetate*, yellow, m. p. 105°; *p-nitrophenylhydrazone*, yellow powder, sintering from 125°, m. p. 134°, decomp. 141°; *acetate*, yellow, m. p. 90°. When the last was recrystallised from alcohol, small, yellow crystals, m. p. 226°, were obtained, but were not identified. The *phenylhydrazone* forms a *m-chloropiperic*ate, m. p. 154-165° (decomp.). Acetylcinchoninal also forms a compound with ammonia and one with sodium hydrogen sulphite.

Benzoylcinchonine ozonide forms a white, voluminous mass decomposing at about 100°. Benzoylcinchoninal is a white substance, m. p. 130° (decomp.);  $[\alpha]_D^{25} -72.4^\circ$ . Its *mono-m-chloropiperic*ate forms greenish-yellow crystals, m. p. 165°, and the *di-m-chloropiperic*ate, yellow crystals, m. p. 165°. The *phenylhydrazone* is amorphous, yellow, m. p. 117-118°, *acetate*, m. p. 127°; *p-bromophenylhydrazone*, orange, amorphous, m. p. 120-122°, *acetate*, m. p. 112-114°; *p-nitrophenylhydrazone*, yellow, m. p. 126-127°.

127° (decomp.), *acetate*, m. p. 130—131°. An aldehyde-ammonia compound is indicated.

*Acetylquinine ozonide* forms a very voluminous, white mass, softening at 75°, decomposing at 90—105° with evolution of gas. *Acetylquininal* is a white substance, m. p. about 120° (decomp.),  $[\alpha]_D^{25} - 63.5^\circ$ . It forms a *mono-m-chloropicate*, greenish-yellow, m. p. 166° (decomp.), and a *di-m-chloropicate*, yellow, softening and decomposing from 138°. The *phenylhydrazone* is a yellow substance, m. p. about 125°, *acetate*, very hygroscopic, yellow, m. p. 65°; *p-bromophenylhydrazone*, yellow, m. p. 120°; *p-nitrophenylhydrazone*, yellow, m. p. 125°. *Acetylquininalammonia* is a white powder, m. p. 82—85°.

*Benzoylquinine ozonide* is a voluminous, white mass, m. p. 95—100°. *Benzoylquininal* is a white substance, m. p. 126°;  $[\alpha]_D^{25} + 79.4^\circ$ ; *mono-m-chloropicate*, greenish-yellow, m. p. 142° (decomp.); *di-m-chloropicate*, yellow, blackening at 155°. The *phenylhydrazone* is a yellow powder, softening from 116°, m. p. 128°, *acetate*, m. p. 118°; *p-bromophenylhydrazone*, yellow, m. p. about 125°, *acetate*, softens at 118—119° (decomp.); *p-nitrophenylhydrazone*, yellow, m. p. 122—133°, *acetate*, m. p. 112—115° (decomp.).

*Benzoylquininal-ammonia* is a white substance, m. p. 131—132°, containing 1 mol. of ether. When prepared in benzene solution it separates with 1 mol. of benzene, m. p. 136—139°.

*Cinchonine ozonide* is a white, amorphous substance, not very voluminous, decomposing at 105°. *Cinchoninal*,  $C_{15}H_{29}O_4N_2$ , is a white, amorphous substance, m. p. 143—145°,  $[\alpha]_D^{25} + 100.5^\circ$ ; it readily reduces Fehling's solution and silver nitrate. It forms a *mono-m-chloropicate*, greenish-yellow crystals, decomposing slowly at 151°, and a *di-m-chloropicate*, decomp. at 155°. The *phenylhydrazone* is amorphous, m. p. 130—135°, and decomposes violently at 140°; *p-bromophenylhydrazone*, yellow, m. p. 120°; *p-nitrophenylhydrazone*, m. p. 130—132° (decomp.). These three hydrazones do not form acetates.

*Quinine ozonide* is a white, amorphous substance decomposing at 109°. *Quininal*,  $C_{19}H_{29}O_4N_2$ , forms small colourless crystals, m. p. 160°, having strong reducing properties,  $[\alpha]_D^{25} - 30^\circ$ . The *mono-m-chloropicate* forms yellow crystals, m. p. 130°; *di-m-chloropicate*, a yellow, vitreous substance, m. p. 126° (decomp.). The *phenylhydrazone* has m. p. 145—147°; *p-bromophenylhydrazone*, yellow, m. p. 125—130° (decomp.). Quininal does not form compound with ammonia, but forms an additive compound with sodium hydrogen sulphite in alcohol, decomposed by water.

E. H. R.

**The Synthesis of Ephedrine.** E. FOURNEAU and J. PUYE (*Anal. Fis. Quim.*, 1922, 20, 394—399; cf. Späth, A., 1921, i, 45; Fournau, A., 1905, i, 57; Eberhard, A., 1915, i, 834).—Ephedrine is obtained from phenylethylcarbinol by the following reactions: Dehydration of phenylethylcarbinol gives propenylbenzene; by the action of bromine water, the corresponding bromohydrin is

obtained, b. p. 145—155°/25 mm. By heating the bromohydrin with a 10% methylamine solution in a sealed tube at 120° for three hours, phenyl- $\alpha$ -methylaminoethylcarbinol (ephedrine) is obtained and separated by appropriate methods. After recrystallisation, colourless prisms are obtained, m. p. 60°. The hydrochloride gives m. p. 180°, subsequently rising to 190°. The stereoisomeric  $\psi$ -ephedrine is obtained from ephedrine hydrochloride by way of acetylation of the latter compound, whereby acetyl  $\psi$ -ephedrine is obtained as colourless crystals, m. p. 176°. Acetyl  $\psi$ -ephedrine, by treatment with hydrochloric acid, gives a  $\psi$ -ephedrine hydrochloride, m. p. 175°, from which the base, m. p. 117°, is obtained.

G. W. R.

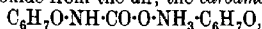
**The Influence of Papaverine on the Optical Activity of Narcotine in Acid Solution.** HAROLD EDWARD ANNETT (T., 1923, 123, 376—379).

[Scopoline. VI. The Constitutions of Scopolamine and Scopoline. The Hofmann Degradation of Scopoline.] J. ADAMER (*Ber.*, 1923, 56, [B], 130—131).—A criticism of the recent communication of Hess and Wahl (A., 1922, i, 854).

H. W.

**Furylethylamine.** YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1922, 1084—1090).—According to the method of Claisen (A., 1905, i, 286), furfuraldehyde (12 g.) and ethyl chloroacetate (15 g.) were condensed in cold absolute ethereal solution by the aid of metallic sodium (3.5 g.) yielding ethyl furyl-glycidate,  $C_4OH_3CH < \begin{smallmatrix} O \\ CH-CO_2Et \end{smallmatrix}$ , b. p. 114—117°/5 mm. The

ester was saponified with alcoholic potash; the resulting potassium salt was dissolved in water, to which the calculated quantity of hydroxylamine hydrochloride was added when the resulting oxime separated as an oil (Rosenmund and Dornsaft, A., 1920, i, 56). *Furylacetaldoxime*,  $C_4OH_3CH_2CH:N\cdot OH$ , b. p. 90—92°/4 mm., is a light yellow, viscid liquid having a strongly sweet taste (about fifty times that of sucrose). When kept, the oily oxime (*anti*-form) gradually changes into the crystalline stable form (*syn*-form), m. p. 64°, the sweetness being reduced by half. By reduction with 3% sodium amalgam and 50% acetic acid in methyl-alcoholic solution, the oxime is converted into *furylethylamine*,  $C_4OH_3CH_2CH_2\cdot NH_2$ , a colourless liquid, b. p. 155°/762 mm.,  $n_D^{20}$  1.0080,  $n_D^{25}$  1.47994; it has a strongly amine-like odour and absorbs carbon dioxide from the air, the *carbamate*,



m. p. 87°, being formed. The *benzoate* has m. p. 81°. K. K.

**Methylisopyromucic Acid and a Method of Characterising Acids of the Sugar Group.** L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1922, 175, 1208—1211; cf. Chavanne, A., 1905, i, 77).—As *isopyromucic acid* may be prepared by dehydration of a dibasic acid derived from a hexose or of a monobasic acid

derived from a pentose, dehydration of a methyl pentose was effected, the lactone of rhamnose being used. The homologue of isopyromucic acid thus obtained, *methylisopyromucic acid*,  $C_8H_8O_8$ , is of yellow colour, m. p.  $133^\circ$ . Oxidation by the sulpho-chromic mixture shows the presence of a methyl group directly linked to carbon. The acid has a strong reducing action on silver salts and on permanganate. Its *benzoyl* derivative, m. p.  $121^\circ$ , may be prepared by the action of benzoyl chloride either directly or in alkaline solution. It is not a true acid, but rather a phenol,  $CH \begin{smallmatrix} \text{C(OH)CO} \\ \text{CH=CMc} \end{smallmatrix} O$  (cf. Chavanne, A., 1902, i, 637, 690); the coloration with ferric chloride is bluish-green. A method of characterising the acids derived from sugars, details of which are given, depends on the fact that dibasic acids derived from hexoses and monobasic acids derived from pentoses and methyl pentoses give colours with ferric chloride whilst monobasic acids derived from hexoses do not do so. The latter give a positive result after careful oxidation.

H. J. E.

**Selenium Organic Compounds. II. Synthesis of Diarylthiophenes and Diarylselenophenes.** MARSTON TAYLOR BOGERT and PILAR PEREZ HERRERA (*J. Amer. Chem. Soc.*, 1923, **45**, 238—243).—When acetophenoneanil is fused with sulphur at  $220$ — $240^\circ$ , a 28% yield of pure 2:4-diphenylthiophen is obtained. The tollis may be used with equal success, and if substituted acetophenones are used the corresponding diarylthiophenes are obtained. If selenium is used instead of sulphur, the products are diarylselenophenes. The following new compounds are described: *acetophenone-o-tolil*, b. p.  $210$ — $220^\circ/57$  mm.; *p-methylacetophenoneanil*, b. p.  $220$ — $240^\circ/53$  mm.; 2:4-diphenylthiophen-5-mercurichloride, m. p.  $223^\circ$  (corr.); 2:4-diphenylselenophen, m. p.  $112.3^\circ$  (corr.), and its 5-mercurichloride, m. p.  $224^\circ$  (corr.); 2:4-di-p-tolylselenophen, m. p.  $136.3^\circ$  (corr.).

Acetophenonedimethylacetal was prepared by heating together at  $40^\circ$  for several hours methyl orthoformate, acetophenone, anhydrous methyl alcohol, and a trace of concentrated hydrochloric acid. After the mixture had stood for sixteen hours, it was made just alkaline with sodium methoxide and the methyl alcohol distilled off.

W. G.

**Derivatives of Hydroxypyrrole.** ERICH BENARY and RUDOLF KONRAD (*Ber.*, 1923, **56**, [B], 44—52).—Previous attempts to obtain simple hydroxypyrrole derivatives from the hydroxy-esters (Benary and Silbermann, A., 1913, i, 651) by hydrolysis and subsequent removal of carbon dioxide have been unsuccessful on account of the small stability of the pyrrole ring towards alkali hydroxide. Attempts have therefore been made to increase the stability by the introduction of the phenyl group in position 1. The hydrolysis of the esters to the corresponding acids is thus rendered possible, but the subsequent removal of carbon dioxide can only be effected without extensive decomposition if the hydroxyl group is protected by methylation.

Ethyl  $\beta$ -anilinoacrylate is transformed by chloroacetyl chloride in the presence of anhydrous ether and pyridine into a mixture of ethyl  $\beta$ -anilino- $\alpha$ -chloroacetylacrylate,  $\text{NHPh}\cdot\text{CH}_2\text{C}(\text{CO}\cdot\text{CH}_2\text{Cl})\cdot\text{CO}_2\text{Et}$ , needles, m. p.  $83^\circ$ , and ethyl  $\text{N}$ -chloroacetyl- $\beta$ -anilinoacrylate,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\text{CH}\cdot\text{CO}_2\text{Et}$ , colourless prisms, m. p.  $136\text{--}137^\circ$ . The former ester is transformed by a cold alcoholic solution of potassium hydroxide into ethyl 4-hydroxy-1-phenylpyrrole-3-carboxylate,  $\text{NPh}\langle\begin{smallmatrix} \text{CH}_2\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CH}_2\text{C}\cdot\text{OH} \end{smallmatrix}\rangle$ , colourless, matted needles, m. p.  $83\text{--}84^\circ$ .

The corresponding acid crystallises in small rods, m. p.  $172\text{--}174^\circ$  (decomp.), and becomes resinified when heated above its melting point in a vacuum. The hydroxy-ester is converted by amyl nitrite into ethyl 5-oximino-4-keto-1-phenylpyrroline-3-carboxylate, lemon-yellow, hexagonal prisms, decomp. about  $185^\circ$  after softening and gradually melting above  $175^\circ$ ; if an excess of sodium nitrite is gradually added to a solution of the ester in glacial acetic acid, an isomeric product,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2$ , almost colourless, coarse needles, m. p.  $157\text{--}158^\circ$ , is formed, the constitution of which has not been elucidated. 4-Acetoxy-1-phenylpyrrole-3-carboxylic acid, colourless needles, m. p.  $145\text{--}147^\circ$ , is produced from the hydroxy-acid, acetic anhydride, and anhydrous sodium acetate; when heated at the atmospheric pressure or in a vacuum, it loses carbon dioxide and acetic acid, and leaves a black, resinous residue. Ethyl 4-hydroxy-5-benzeneazo-1-phenylpyrrole-3-carboxylate, orange-yellow needles, m. p.  $170\text{--}172^\circ$ , after previous softening, could not be hydrolysed to the corresponding acid,  $\text{NPh}\langle\begin{smallmatrix} \text{CH}=\text{C}\cdot\text{CO}_2\text{H} \\ \text{C}(\text{N}\cdot\text{NPh})\cdot\text{C}\cdot\text{OH} \end{smallmatrix}\rangle$ ,

which, however, is prepared by the action of benzenediazonium chloride on an alkaline solution of the hydroxy-acid; it crystallises in orange-coloured needles, m. p. about  $185\text{--}187^\circ$  after softening at  $175^\circ$ . It is decomposed with loss of aniline when heated in a vacuum. 4-Methoxy-1-phenylpyrrole-3-carboxylic acid is prepared by the action of methyl sulphate on the hydroxy-acid and subsequent hydrolysis of the methyl ester; it forms leaflets, m. p.  $166\text{--}167^\circ$  (decomp.) [the potassium salt, long, colourless needles, is described]. The acid loses carbon dioxide when heated in a vacuum at  $180\text{--}200^\circ$ , and yields 3-methoxy-1-phenylpyrrole,  $\text{NPh}\langle\begin{smallmatrix} \text{CH}_2\text{C}\cdot\text{H} \\ \text{CH}_2\text{C}\cdot\text{OMe} \end{smallmatrix}\rangle$ , colourless needles, m. p.  $33\text{--}34^\circ$ , which when molten or dissolved rapidly become brown on exposure to air. Attempts to hydrolyse the methoxyl to the hydroxyl group by aluminium chloride, hydrogen chloride, or hydrogen bromide were unsuccessful owing to the instability of the free hydroxypyrrole.

Methyl  $\beta$ -anilino- $\alpha$ -chloroacetylcrotonate is converted by potassium hydroxide in methyl alcoholic solution into methyl 4-hydroxy-1-phenyl-2-methylpyrrole-3-carboxylate,  $\text{NPh}\langle\begin{smallmatrix} \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{Me} \\ \text{CH}=\text{C}\cdot\text{OH} \end{smallmatrix}\rangle$ , small needles, m. p.  $123\text{--}124^\circ$ ; the corresponding acid crystallises in colourless needles, m. p.  $145^\circ$ . The hydroxy-ester is converted by amyl nitrite into methyl 5-oximino-4-keto-2-methyl-1-phenyl-

*pyrroline-3-carboxylate*,  $C_{13}H_{13}O_4N_2$ , pale yellow needles, m. p. 185–187° (decomp.), from which the corresponding acid,  $C_{15}H_{15}O_4N_2$ , small, pale yellow needles, m. p. 171–172° (decomp.), is obtained. Sodium nitrite converts the hydroxy-ester dissolved in glacial acetic acid into *methyl 5-nitroimino-4-keto-1-phenyl-2-methylpyrroline-3-carboxylate*, orange-coloured needles, m. p. 192–193° (decomp.) after previous softening. H. W.

**The Action of Diazomethane on Dyes and certain Nitro-pyrroles.** WILLIAM KÜSTER and WILHELM MAAG (*Ber.*, 1923, 56, [B], 55–69).—It has been shown previously (Küster, A., 1922, i, 885) that the action of diazomethane on bilirubin leads to the introduction of two methyl groups into the molecule and in addition a molecule of diazomethane is combined, forming a compound,  $C_{36}H_{42}O_6N_8$ . A further investigation of this compound and comparison of its properties with those of substances obtained by the action of diazomethane on pyrrole derivatives led the authors to the conclusion that a portion of the bilirubin molecule must contain the pyrrolenylmethanepyrrol group.

The product,  $C_{36}H_{42}O_6N_8$ , of the addition of diazomethane to esterified bilirubin is a red, amorphous powder which contains three methyl groups eliminable by hydriodic acid. It can be prepared in a crystalline form resembling bilirubin by the action of diazomethane on pure bilirubin and bilirubinammonia suspended in anhydrous ether; it, however, passes readily into the resinous variety.

Indigoid ethyl bis-2-methylpyrroline-3-carboxylate (Benary and Silbermann, A., 1913, i, 652) contains two carbethoxy-groups which are readily hydrolysed by hydriodic acid at 140°, whereas a further evolution of alkyl iodide is not observed below 300°; it is converted by diazomethane in the presence of ether into a red resin.

*Methyl 5-3'-acetyltetronylidene-4-keto-2-methylpyrrole-3-carboxylate*,  $CO_2Et-C-CO > C-C < CH_2-CH_2-O$   
 $Me-C-NH > C-C < C(CMe-OH)-CO$  yellow needles, m. p. 190°

(decomp.), is prepared by the action of alcoholic potassium hydroxide solution on a mixture of acetyltetronamide and ethyl chloroacetylaminocrotonate; it is converted by diazomethane into a reddish-brown resin,  $C_{16}H_{19}O_6N$ , m. p. 75° (decomp.).

Ethyl 5:5'-bis-4-keto-2-methylpyrroline-3-carboxylate hydrate,  $C_{16}H_{20}O_6N_2.H_2O$  (cf. Benary and Silbermann, *loc. cit.*), loses two ethyl groups under the action of hydriodic acid at 140°, and does not suffer further loss of alkyl iodide below 340°; it is converted by diazomethane into a yellow, brittle resin,  $C_{18}H_{24}O_5N_2$ , m. p. 73–74° (decomp.).

3-Hydroxy-4-carbethoxy-5-methylpyrrolenyl-2-furylmethane,  $C_{13}H_{13}O_4N$  (Küster, A., 1922, i, 858), combines with hydrogen chloride in the presence of acetone to form a *hydrochloride*,  $C_{13}H_{14}O_4NCl$ , rust-brown needles, which readily lose hydrogen chloride on exposure to air. The substance is converted by diazomethane into a dark brown resin. 3-Hydroxy-4-carbethoxy-5-methyl-2-o-pyrrolenylhydroxyphenylmethane, brownish-yellow needles,

m. p. 207° (decomp.), is readily prepared from Benary's pyrrole and salicylaldehyde, and is transformed by diazomethane into a yellow resin, m. p. about 40° after previous darkening.

Ethyl 2 : 5-dimethylpyrrole-3-carboxylate is oxidised by chromic acid to *carbethoxymaleinimide*,  $C_7H_7O_4N$ , colourless needles, m. p. 115°.

Benary's indigoid pyrrole (*loc. cit.*) is oxidised by nitric acid (*d* 1.4) at 0° to ethyl 5-nitro-2 : 4-dihydroxypyrrrole-3-carboxylate, colourless needles, decomp. 100°. The potassium salt,  $C_7H_7O_6N_2K$ , decomp. 167°, barium salt, decomp. 165°, lead, and copper salts are described. Hydrogen sulphide reduces the nitro-compound to a colourless substance, m. p. 121°. The ester is readily hydrolysed to 5-nitro-2 : 4-dihydroxypyrrrole-3-carboxylic acid, colourless needles, decomp. 124°, the ammonium and silver salts of which are described; the methyl ester crystallises in colourless needles, decomp. 112°. Ethyl 5-nitro-2-hydroxy-4-methoxypyrrrole-3-carboxylate, a pale yellow liquid, b. p. 146°, which solidifies to needle-shaped crystals when cooled with ice, is readily prepared by the action of diazomethane on the corresponding dihydroxy-ester. 5-Nitro-2-hydroxy-4-methoxypyrrrole-3-carboxylic acid crystallises in colourless needles; the ammonium salt, silver salt, and the methyl ester, a colourless liquid, b. p. 145°, are described.

Ethyl 5-nitro-4-hydroxy-2-methylpyrrole-3-carboxylate, colourless needles, m. p. 100.5° (decomp.), is readily hydrolysed to 5-nitro-4-hydroxy-2-methylpyrrole-3-carboxylic acid, colourless needles, decomp. 124°. It is converted by diazomethane into ethyl 5-nitro-4-methoxy-2-methylpyrrole-3-carboxylate. H. W.

**The Tetrachlorodipyridinoiridates. Configurations of the Two Series of Iridiumdipyridinotetrachloro-compounds.** MARCEL DÉLÉPINE (*Compt. rend.*, 1922, 175, 1211—1213; cf. this vol., i, 135).—These are neutral un-ionised substances. *cis*- and *trans*-Isomerides exist which are derived from the orange and red salts, respectively. They are not of equal stability towards oxidising agents, and are themselves of unequal oxidising power. Both decompose iodides according to the equation  $Ir(C_5H_5N)_2Cl_4 + MI \rightarrow Ir(C_5H_5N)_2Cl_4M + I$ , but only the *cis*-compound decomposes bromides. This is consistent with the fact that bromine can be used only in preparing the orange salts. The author concludes that the *cis*-isomeride behaves as a halogen intermediate between chlorine and bromine, and the *trans* as intermediate between bromine and iodine. The constitution was determined by reason of the dichroism of the chloride derived from the orange salt, which is isomorphous with and confers the property of dichroism on platinum tetrachlorodipyridine,  $PtCl_4(C_5H_5N)_2$ . It has been shown (Werner and Fassbender, A., 1897, i, 631; Jörgensen, A., 1901, i, 163) that the latter substance has the *cis*-configuration, hence the same configuration is inferred for the orange salts. The red salts have, therefore, the *trans*-configuration. H. J. E.

#### β-Ketonic Nitriles and their Relation to Cyclic Compounds.

E. P. KOHLER and B. L. SOUTHER (*J. Amer. Chem. Soc.*, 1922, 44, 2903—2914; cf. this vol., i, 54).—Cyanoacetamide and cyano-

acetonitrile, like methyl cyanoacetate, condense with phenyl styryl ketone, but the three products, although closely related, behave differently towards most reagents. All three form cyclic compounds under the influence of halogen acids in indifferent media. The product from methyl cyanoacetate forms a tetrahydropyridine derivative, in the production of which the cyano-group is involved and molecular rearrangement occurs. The product from cyanoacetamide also forms a tetrahydropyridine derivative, but in its production the amide group is involved. Under the same conditions, the product from the dinitrile forms only a trace of a tetrahydropyridine derivative, the main product being a mixture composed of a pyridine and a hexahydropyridine derivative. This mixture is doubtless due to a series of reactions starting with the addition of halogen acid to one of the cyano-groups and ending with the spontaneous oxidation and reduction of an intermediate dihydropyridine derivative. The results confirm the view that such oxidation-reduction reactions are associated with the extraordinary activity of hydrogen which is in combination with atoms that are flanked on both sides by unsaturated groups; but they do not support the conclusion of Knoevenagel and his co-workers (cf., A., 1903, i, 785) that hydropyridine derivatives are incapable of reacting in all possible desmotropic modifications.

Cyanoacetamide condenses with phenyl styryl ketone under the conditions previously described (*loc. cit.*) to give  $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyramide, m. p. 161–163°, and similarly cyanoacetitrile yields  $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyronitrile, m. p. 125–126°. When dry hydrogen chloride or bromide is passed into a chloroform solution of the above amide, 2-keto-3-cyano-4:6-diphenyltetrahydropyridine, m. p. 220°, is obtained, and this on hydrolysis with concentrated sulphuric acid yields 2-keto-3-carbamyl-4:6-diphenyltetrahydropyridine, m. p. 181–182°, and when treated with nitrous acid gives 1-hydroxy-3-cyano-4:6-diphenylpyridine, m. p. 313–315°. With alcoholic ammonia, the dihydropyridine derivative undergoes spontaneous oxidation-reduction and the products are a hydroxypyridine and 2-keto-3-cyano-4:6-diphenylpiperidine, m. p. 188–189°.  $\alpha$ -Cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyronitrile also reacts with halogen acids in dry chloroform solution. With hydrogen chloride, one of the products is 2-chloro-3-cyano-4:6-diphenylpyridine, m. p. 154.5°, and with hydrogen bromide 2-bromo-3-cyano-4:6-diphenylpyridine, m. p. 169–170°, is obtained. In the latter reaction a red oil was also formed from which after pouring it into a solution of sodium hydrogen carbonate 2-keto-3-carbamyl-4:6-diphenylpiperidine, m. p. 170°, was isolated, and this on treatment with hydrogen chloride in methyl alcohol gave methyl 2-keto-4:6-diphenylpiperidine-3-carboxylate, m. p. 177°.

With alkalis, the cyanoamide additive product, m. p. 161–163°, described above, is transformed into its cyclic isomeride, the only other product being a trimolecular compound. With alcoholic alkalis, the dinitrile additive product gives pyridyl ethers, of which 2-methoxy-3-cyano-4:6-diphenylpyridine, m. p. 110°, and 2-ethoxy-3-cyano-4:6-diphenylpyridine, m. p. 112°, were prepared.

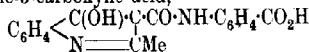
The rearrangement of the cyanoacetamide additive product to cyclic compounds takes place so easily that only cyclic bromo-compounds were obtained from it, even when the bromination was carried out in the presence of potassium acetate. From the dinitrile, however, it was possible to obtain one open-chain bromo-compound by brominating it in the presence of potassium acetate. The behaviour of this substance towards halogen acids confirms the view previously expressed (*loc. cit.*) regarding the mechanism by which bromopyridine derivatives are formed when bromine acts on open-chain ketonic nitriles, since when dry hydrogen chloride is passed into a chloroform solution of the bromo-compound the product is a chloropyridine derivative. The compounds described are:  $\alpha$ -bromodi- $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyronitrile, m. p. 126–127°, 5-bromo-2-keto-3-cyano-4 : 6-diphenyltetrahydropyridine, m. p. 165°, 5-chloro-2-keto-3-cyano-4 : 6-diphenyltetrahydropyridine, m. p. 178–181°, 3 : 5-dibromo-2-keto-3-cyano-4 : 6-diphenyltetrahydropyridine, m. p. 195° (decomp.), 5-bromo-2-hydroxy-3-cyano-4 : 6-diphenylpyridine, m. p. 303–306° (decomp.), 2-chloro-5-bromo-3-cyano-4 : 6-diphenylpyridine, m. p. 181–182°, and 2 : 5-dibromo-3-cyano-4 : 6-diphenylpyridine, m. p. 189–190°. W. G.

**The Ethoxyquinaldines.** W. T. K. BRAUNHOLTZ (*J. Amer. Chem. Soc.*, 1922, **44**, 2967; cf. T., 1922, **121**, 169).—In reference to a paper by Gutekunst and Gray (A., 1922, i, 950), the author directs attention to the preparation and description of the 5-, 6-, and 7-ethoxyquinaldines by himself (*loc. cit.*). W. G.

**The Constitution of Dianhydrodiacetylanthranilic Acid.** GUSTAV HELLER and HERBERT GRUNDMANN (*Ber.*, 1923, **56**, [B], 200–205).—The action of phosphoryl chloride on acetylanthranilic acid or its esters or on acetylanthranil has yielded a compound which Anschütz and Schmidt (A., 1903, i, 56) designate dianhydrodiacetylanthranilic acid, and to which they assign the constitution

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH}) \end{array} \text{C}_6\text{H}_4 \text{ or } \text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N} \\ \text{N}\cdot\text{CO}\cdot\text{CH}_2\cdot(\text{HO})\text{C} \end{array} \text{C}_6\text{H}_4.$$

This compound has now been obtained incidentally by the action of acetic anhydride on benzene- or *p*-toluene-sulphonylanthranilic acid, and is shown to be the *o*-carboxyanilide of 4-hydroxy-2-methylquinoline-3-carboxylic acid,



*p*-Toluenesulphonylanthranilic acid is converted by boiling acetic anhydride into the mixed *anhydride* of toluene-*p*-sulphonic acid and the *o*-carboxyanilide of 4-hydroxy-2-methylquinoline-3-carboxylic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH})\cdot\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me} \\ \text{N}=\text{CMe} \end{array}$ , pale yellow crystals, m. p. 214–215° (decomp.). The substance is decomposed by dilute sodium hydroxide solution into the *o*-carboxyanilide of 4-hydroxy-2-methylquinoline-3-carboxylic acid, m. p. 249–250° (decomp.), identical with the product obtained by Anschütz and Schmidt (*loc. cit.*). It is converted by glacial acetic

and concentrated hydrochloric acids at 130—140° into 4-hydroxy-2-methylquinoline. A substance,  $C_{13}H_{13}O_2N_2S$ , slender needles, m. p. 133.5°, is obtained as by-product of the action of acetic anhydride on *p*-toluenesulphonylanthranilic acid. It appears to contain acetic anhydride and solvent of crystallisation; when deprived of this it has m. p. 159—160° (decomp.), but the amount of it available was insufficient for an extended examination.

Benzenesulphonylanthranilic acid is transformed by boiling acetic anhydride into the mixed *anhydride*,  $C_{15}H_{13}O_5NS$ , slender needles, m. p. 157—158°.

*p*-Toluenesulphonylanthranilic acid is transformed by glacial acetic and concentrated hydrochloric acids at 140° into *anthranilic acid toluene-p-sulphonate*,  $C_{14}H_{15}O_5NS$ , slender needles, m. p. 218° (decomp.). The corresponding benzenesulphonate has m. p. 230° (decomp.). H. W.

**The Constitution of Naphtholisatin and its Derivatives.** C. CÂNDEA (*Bull. Acad. Sci. Roumaine*, 1922, 8, 31—39).—Colourless condensation products of isatin with  $\alpha$ -naphthol were prepared. These differ from similar compounds obtained from phenols in that they are almost insoluble in alkaline solutions, are not oxidised to coloured substances, and do not form acetyl derivatives. The condensation probably occurs at the 3-position of the indole nucleus (cf. Dănilă and Căndeia, A., 1916, i, 417). The derivatives obtained were: *Di- $\alpha$ -naphtholisatin*,  $C_{28}H_{19}O_3N$ , prismatic needles, m. p. above 300°. *Di- $\alpha$ -naphtholmonobromoisatin*,  $C_{28}H_{18}O_3NBr$ , prismatic needles, m. p. above 300°. *Di- $\alpha$ -naphtholdibromisatin*,  $C_{28}H_{17}O_3NBr_2$ , prismatic needles, m. p. above 300°. *Di- $\alpha$ -naphtholmonochlorisatin*,  $C_{28}H_{18}O_3NCl$ , crystals, m. p. above 300°. *Di- $\alpha$ -naphtholdichloroisatin*,  $C_{28}H_{17}O_3NCl_2$ , prismatic needles, m. p. above 300°. H. J. E.

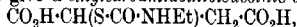
**Stereochemical Studies. VII. 2-Thion-4-methylthiazoline-3-acetic Acid.** BERTIL GROTH and BROR HOLMBERG (*Ber.*, 1923, 56, [B], 289—298).—2-Thion-4-methylthiazoline-3-acetic acid,  $S < \begin{smallmatrix} CS-N-CH_2-CO_2H \\ CH:CM_e \end{smallmatrix}$ , pale honey-yellow, thick plates or short prisms, m. p. 198—199° (decomp.), is prepared in 87% yield by the action of chloroacetone on an aqueous solution of glycine hydrochloride and potassium hydroxide which has been agitated with carbon disulphide until the latter is completely dissolved; it dissolves in water to the extent of 2.06 g. per litre at the atmospheric temperature. The *sodium* salt, rectangular plates (+5H<sub>2</sub>O), *barium* salt, rosettes of needles (+2H<sub>2</sub>O), *methyl* ester, almost colourless needles, m. p. 96—97°, and *ethyl* ester, long, almost colourless needles, m. p. 97—98°, are described. The acid could not be resolved into its optical antipodes by treatment with *l*- or *d*-phenylethylamine in aqueous or alcoholic solution; the salts of the *r*-acid with the optically active bases were isolated (m. p. 161—162° and 160—162°). The acid is unusually stable towards hydrolysis by acid or alkali. It is oxidised by nitric acid (or less

conveniently by bromine water) to the inner anhydride of 2-keto-4-methylthiazoline-3-acetic acid,  $\text{CO} \begin{smallmatrix} \text{CH}_2\text{N}^+\text{CMe} \\ \text{O}-\text{CH}-\text{S} \end{smallmatrix} \text{CH}$ , which is isolated as the hydrogen sulphate,  $\text{C}_6\text{H}_7\text{O}_2\text{SN}_2\text{H}_2\text{SO}_4$ , a colourless, crystalline, somewhat hygroscopic substance, m. p. 114–115°, to a turbid liquid. The corresponding hydrochloride (anhydrous and monohydrate) is described; it has m. p. above 230° (decomp.) after darkening at 200° and becoming black at 230°. The free base is a colourless, crystalline powder (+2.5H<sub>2</sub>O), m. p. 110–115° (decomp.) after softening and becoming discoloured at 95°, m. p. (anhydrous) 165° (decomp.). It is stable in hot aqueous, acidic solution, but is readily decomposed in neutral or alkaline solution with the formation of ill-defined products. It was not found possible to isolate the corresponding acid, since the tendency towards dehydration is so marked that the anhydride can exist even in faintly alkaline solution. H. W.

#### Stereochemical Investigations of the Diketothiazolidines.

I. STEN KALLENBERG (*Ber.*, 1923, 56, [B], 316–331).—In contrast to the  $\psi$ -thiohydantoins and the rhodanines, the diketothiazolidines which have a mobile hydrogen atom attached to the asymmetric  $\beta$ -carbon atom, exhibit normal stereochemical relationships. They can readily be prepared in optically active forms which easily undergo racemisation in consequence of the possibility of desmotropic change.

Potassium ethylthiocarbamate,  $\text{NHEt}\cdot\text{CO}\cdot\text{SK}$ , is prepared conveniently by the action of carbon oxydisulphide on a solution of potassium hydroxide and ethylamine hydrochloride in absolute alcohol. Under certain conditions, particularly with regard to concentration, it reacts with a solution of sodium *l*-bromosuccinate in cold water to give *d*-ethylcarbamidothiolsuccinic acid,



small plates,  $[\alpha]_D +103.5^\circ$  in absolute alcoholic solution. The acid is readily decomposed by concentrated ammonia with the production of *d*-thiomalic acid, by warm acids to *d*-thiomalic acid, carbon dioxide, and ethylamine, on the one hand, and to *r*-diketo-ethylthiazolidineacetic acid,  $\begin{smallmatrix} \text{NEt}\cdot\text{CO} \\ \text{CO}-\text{S} \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , on the

other, by alkalis into *d*-thiomalic acid, carbon dioxide, and amine. *r*-Ethylcarbamidothiolsuccinic acid crystallises in colourless, thin prisms or short needles, m. p. 141–142° (decomp.).

The action of cold concentrated hydrochloric acid on *d*-ethylcarbamidothiolsuccinic acid gives a mixture of *r*-diketoethylthiazolidineacetic acid, colourless prisms, m. p. 113–115°, and the corresponding *d*-acid which, however, could not be caused to crystallise. The racemic acid can be resolved with the aid of active phenyl-ethylamine, but the active acids are again obtained only in the form of non-crystalline syrups.

*d*-Methylcarbamidothiolsuccinic acid, prepared from potassium methylthiocarbamate and sodium *l*-bromosuccinate, has m. p. 114–116° (decomp.),  $[\alpha]_D +99.2^\circ$  in absolute alcoholic solution.

The corresponding *r*-acid crystallises in colourless, spherical aggregates, m. p. 135—136° (decomp.). The active acid is converted by concentrated hydrochloric acid into *d*-diketomethylthiazolidineacetic acid, transparent prisms, m. p. 101—102°,  $[\alpha]_D +208.0^\circ$  in absolute alcoholic solution (the success of the reaction greatly depends on the conditions of the experiment, which are described in detail in the original). It is converted in alkaline solution into *r*-methyl-carbamidothiolsuccinic acid. Since *d*-methylcarbamidothiolsuccinic acid is not racemised under similar conditions, it follows that *d*-diketomethylthiazolidineacetic acid must be converted into the corresponding *r*-compound previously to fission of the thiazole ring. Preliminary measurements show that the velocity of racemisation is diminished with increasing concentration of hydrogen-ions and increased by increasing concentration of hydroxyl-ions. *r*-Diketomethylthiazolidineacetic acid crystallises in small, colourless plates, m. p. 98—99°.

*d*-Dimethylcarbamidothiolsuccinic acid forms colourless prisms, m. p. 138—139° (decomp.),  $[\alpha]_D +81.7^\circ$  in absolute alcoholic solution. It is decomposed by hot *N*-sodium hydroxide solution to a small extent into thiomalic acid, carbon dioxide, and dimethylamine, but the greater portion is constitutionally unchanged and only slightly racemised. Similar treatment with *N*-sulphuric acid causes an almost complete fission into partly racemised thiomalic acid; concentrated hydrochloric acid at the atmospheric temperature gives the same result, except that fission is less extensive and racemisation of the products more pronounced.

H. W.

**The Tautomerism of Amidines. I. 2:4- and 2:5-Diphenylglyoxalines.** RICHARD BURTLES and FRANK LEE PYMAN (T., 1923, 123, 361—367).

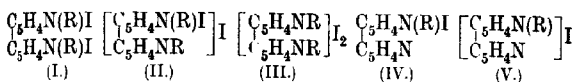
**The Tautomerism of Amidines. II. The Alkylation of Open-chain Amidines.** FRANK LEE PYMAN (T., 1923, 123, 367—370).

**Some New Hypnotics of the Barbituric Acid Series.** H. A. SHONLE and A. MOMENT (*J. Amer. Chem. Soc.*, 1923, 45, 243—249).—Various dialkyl- and alkylaryl-barbituric acids were prepared and tested for hypnotic action. The monoalkyl- and aryl-derivatives were found to be inactive in doses of 0.5 to 1 g. per kg. of body weight when injected subcutaneously in rabbits. Dimethylbarbituric acid was without any apparent action on rabbits in a dose of 0.75 g. per kg. of body weight. Then as the molecular weight increased the activity increased until a maximum was reached, after which it declined until the hypnotic activity was lost and the animal showed only muscular inco-ordination or no effect at all, as was the case with dibenzylbarbituric acid. However, the length and type of the carbon atom chains of the entering groups play an important part in modifying the activity. Branched chains are more active and less toxic than are the straight chains. Of the aliphatic compounds investigated, ethylisoamylbarbituric

acid was found to be the most active as well as to possess the lowest toxicity. The relative activities of the barbituric acid derivatives tested are tabulated. New malonic esters prepared are as follows: *ethyl-sec.-butylmalonic ester*, b. p. 155–160°/60 mm.,  $d_{20}^{25}$  0.9858,  $n_D^{25}$  1.4264; *ethylisobutylmalonic ester*, b. p. 119–120°/8 mm.,  $d_{20}^{25}$  0.9682,  $n_D^{25}$  1.4228; *ethylisoamylmalonic ester*, b. p. 150°/20 mm.,  $d_{20}^{25}$  0.9540,  $n_D^{25}$  1.4255; *propylisopropylmalonic ester*, b. p. 143°/42 mm.,  $d_{20}^{25}$  0.9803,  $n_D^{25}$  1.4239; *isopropyl-n-butylmalonic ester*, b. p. 136°/14 mm.,  $d_{20}^{25}$  0.9742,  $n_D^{25}$  1.4291.

New derivatives of barbituric acid are *ethylisobutylbarbituric acid*, m. p. 174–176°, *ethylisoamylbarbituric acid*, m. p. 154–156°, *isopropyl-n-butylbarbituric acid*, m. p. 209–210°, *n-propylisopropylbarbituric acid*, m. p. 161–162°, *isopropylisoamylbarbituric acid*, m. p. 173–175°, *propylisoamylbarbituric acid*, m. p. 129–132°, *ethyl-sec.-butylbarbituric acid*, m. p. 155–157°. W. G.

**The Colour of the 2:2'-Dipyridylum Halogenides.** BRUNO EMMERT and JULIUS STAWITZ (*Ber.*, 1923, 56, [B], 83–91).—An extensive series of 4:4'-dipyridylum di- and mono-alkyl halides has been examined. The various colours which they exhibit in substance and when dissolved and the failure of their solutions to observe Beer's law, are explained by the application of Hantzsch's views on the constitution of ammonium salts.



The constitution I is ascribed to the red dipyridylum di-iodides and the corresponding pseudo-form, IV, to the yellow monoiodides. The yellow hydrates of the di-iodides have the constitution II, whereby the difference between their colour and that of the anhydrous compounds and their similarity with the monoiodides is explained. In the aqueous and alcoholic solutions of the di-iodides, the three forms, I, II, and III, are present in equilibrium, the two latter being electrolytically dissociated. In a similar manner, the failure of the monoiodides to obey Beer's law in solution is explained by the equilibrium between the yellow molecules (IV) and the colourless molecules (V).

The following individual compounds are described: 4:4'-*Dipyridyl dihydriodide*, red prisms, and the corresponding *mono-hydriodide* (golden-yellow prisms, +1H<sub>2</sub>O and anhydrous). The corresponding *dihydrobromide*, long, pale yellow needles, *mono-hydrobromide*, colourless, prismatic needles (+H<sub>2</sub>O), and *mono-hydrochloride* (+H<sub>2</sub>O). 4:4'-*Dipyridyl monomethiodide*, a pale yellow, crystalline powder, and the corresponding *hydriodide*. 4:4'-*Dipyridyl dimethobromide*, yellow prisms. 4:4'-*Dipyridyl diethiodide*, orange-coloured prisms, and the corresponding *mono-ethiodide*, lustrous, yellow leaflets. 4:4'-*Dipyridyl dipropiodide*, red crystals, which yields a *pentahydrate* on exposure to moist air, the *monopropiodide*, yellow crystals, the *dipropobromide*, greenish-yellow crystals, and the *dipropochloride*, colourless, lustrous leaflets.

which deliquesce on exposure to air. 4:4'-Dipyridyl methiodide propiodide, red, oblique prisms. 4:4'-Dipyridyl monoisobutiodide, which closely resembles the monopropiodide. 4:4'-Dipyridyl monoisoamyliodide. 4:4'-Dipyridyl di-sec.-hexyliodide, a brownish-red substance, di-hydrate, yellow needles. 4:4'-Dipyridyl di-benzyliodide, a red substance which gives an unstable, yellow hydrate, dibenzylbromide and the corresponding pale yellow tetrahydrate.

H. W.

Some Derivatives of Methylenediquinaldine and their Relationship to the Carbocyanines. FRANCES MARY HAMER (T., 1923, 123, 246—259).

The Colour of Di- and Tri-2-quinolylmethanes and their Derivatives. GÜNTHER SCHEIBE (*Ber.*, 1923, 56, [B], 137—148; cf. A., 1921, i, 62, 451; 1922, i, 1190).—Di- and tri-2-quinolylmethanes exist in colourless and coloured forms which yield an equilibrium mixture in solution or in the molten condition. The former varieties can be represented satisfactorily by formulæ of the type  $\text{CH}_2(\text{C}_9\text{H}_6\text{N})_2$ , but the coloured compounds do not possess the quinonoid structure,  $\text{C}_9\text{H}_6\text{N}:\text{CH}:\text{C}_9\text{H}_6\text{N}:\text{NH}$ , since their absorption spectra differ entirely from those of the 1-alkyl derivatives. The hydrogen atom is not attached directly to the central carbon atom or to either nitrogen atom, but as it is shown by the chemical reactions of the compounds to be related to all three, it must be ascribed a position within their sphere of influence. The optical effect of this mode of union of the hydrogen appears to be similar to that of the union of the anion in the dye salts, although it is not ionisable. In this case, ionisation does not appear to have an immediate relationship to optical properties.

[With R. PFLOCK, K. SCHOLL, and E. FRIEDEL].—Di-2-quinolylmethane is prepared without particular difficulty by the process described recently (A., 1922, i, 1190); the success of the operation depends on the presence of small quantities of hydrogen chloride such as are usually retained by 2-chloroquinoline. König's failure to prepare the compound (A., 1922, i, 1188) is due to the use of too carefully purified materials.

A cold solution of di-2-quinolylmethane in alcohol is converted by four molecular proportions of nitric acid into the dinitrate,  $\text{C}_{18}\text{H}_{14}\text{N}_2\cdot 2\text{HNO}_3$ , colourless, lustrous leaflets. The salt is converted when heated by itself or in alcoholic solution into nitro-di-2-quinolylmethane mononitrate,  $\text{NO}_2\cdot\text{CH}(\text{C}_9\text{H}_6\text{N})_2\cdot\text{HNO}_3$ , yellow plates, decomp.  $145^\circ$ ; this is converted by sodium hydroxide into a colourless, crystalline substance, which, after desiccation in a toluene bath, gives the sodium salt of the mononitro-compound,  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_3\text{Na}$ , yellow crystals, m. p.  $282^\circ$ . Nitro-di-2-quinolylmethane crystallises in yellow needles, m. p.  $200^\circ$ . It appears to yield only monoacid salts even with an excess of mineral acid. It is converted by nitric acid in warm glacial acetic acid solution into dinitro-di-2-quinolylmethane,  $\text{C}(\text{C}_9\text{H}_6\text{N})_2(\text{NO}_2)_2$ , almost colourless prisms, m. p.  $140^\circ$ .

Tri-2-quinolylcarbinol is converted by acetic anhydride and

sodium acetate into the corresponding *acetate*,  $C_{30}H_{21}O_2N_3$ , colourless prisms, m. p.  $190^\circ$ .

Bromine and tri-2-quinolylmethane yield *tri-2-quinolylbromomethane*,  $C_{28}H_{18}N_3Br$ , colourless crystals, m. p.  $169^\circ$ . It gives a *di-picrate*, and is converted by alcoholic potassium hydroxide solution into *tri-2-quinolylmethyl ethyl ether*, colourless crystals, m. p.  $179^\circ$ , and a compound of high melting point which appears to be the ether derived from two molecules of the carbinol. It is smoothly reduced by phenylhydrazine in the presence of benzene to tri-2-quinolylmethane.

*p*-Dimethylaminobenzylidenepicoline forms pale yellow crystals, m. p.  $139^\circ$ , and, like the corresponding quinaldine derivative, gives coloured salts with acids, which are immediately decomposed by alkali. Nitrous acid appears to transform the compounds into nitroso-amines, but the investigation of these substances is not complete.

When molecular proportions of acetylacetoneanil, aniline, and zinc chloride are warmed with a little alcohol, the additive compound of the dianil with zinc chloride,  $C_{17}H_{18}N_2 \cdot ZnCl_2$ , colourless prisms, decomp.  $256^\circ$ , is obtained. This suffers decomposition into the monoanil when treated with ammonia. The *dianil monohydrochloride*, yellow prisms, m. p.  $218^\circ$ , is prepared from the monoanil and aniline hydrochloride, but it was not found possible to obtain the crystalline base from the salt.

Acetylacetonecarbamide (cf. Stark, A., 1909, i, 260) which has been prepared in the light and is therefore yellow, melts at  $95^\circ$  to a colourless liquid which re-solidifies at about  $100^\circ$ , becomes yellow when further heated, and has m. p.  $198^\circ$ . Dibenzylideneacetylacetonecarbamide yields a *monohydrochloride*,  $C_{30}H_{17}ON_2Cl$ .

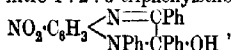
H. W.

### Contraction of the Ring in the Cases of Quinoxaline Derivatives and a New Method of Formation of Benziminazoles. I.

K. BRAND and E. WILD (*Ber.*, 1923, 56, [B], 105—119).—The condensation of the hydrochlorides of *N*-mono-substituted aromatic *o*-diamines with 1 : 2-dicarbonyl compounds leads in general to the production of quinoxaline derivatives. It is therefore remarkable that benzil and 4-nitro-2-aminophenyl-*p*-tolylamine in the presence of hydrochloric acid yield 5-nitro-2-phenyl-1-*p*-tolylbenziminazole hydrochloride in place of the expected stilbazonium chloride, the 5-membered iminazole ring being formed in place of the expected 6-membered diazine ring. A number of possibly similar instances have also been examined.

5-Nitro-2-phenyl-1-*p*-tolylbenziminazole hydrochloride, colourless, slender needles, m. p.  $235^\circ$ , readily separates when a solution of benzil and 4-nitro-2-amino-4'-methyl-diphenylamine in alcohol is boiled with hydrochloric acid.

Benzil-5-nitro-2-anilinoanil,  $COPh \cdot CPh \cdot N \cdot C_6H_3(NO_2) \cdot NHPh$ , pale yellow needles, m. p.  $205^\circ$ , is slowly converted by sulphuric acid into the  $\psi$ -base of 6-nitro-1 : 2 : 3-triphenylstilbazonium,



m. p. 161°, which is more conveniently prepared by the action of hydrochloric acid on the anil under conditions which are described in detail in the original communication. The anil is transformed by treatment with concentrated hydrochloric acid in boiling alcoholic solution into 5-nitro-1:2-diphenylbenziminazole, m. p. 181° (cf. Walther and Kessler, A., 1906, i, 898); the latter substance is also prepared by the action of hydrochloric acid and alcohol on 6-nitro-1:2:3-triphenylstilbazonium base and from benzil and 4-nitro-2-aminodiphenylamine under somewhat similar conditions.

The 6-chloro-1:2:3-triphenylstilbazonium  $\psi$ -base, yellow needles, m. p. 164°, prepared by the condensation of benzil and 4-chloro-2-aminodiphenylamine in boiling alcoholic solution could not be converted into 5-chloro-1:2-diphenylbenziminazole by treatment with alcohol and hydrochloric acid, even after addition of nitrobenzene to the mixture.

6-Nitro-2:3-diphenylquinoxaline is unchanged when heated at 150–170° with alcohol and hydrochloric acid.

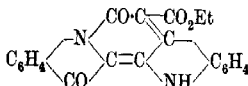
According to the conditions, particularly with respect to the amount of acid used, the action of 4-nitro-2-amino-*N*-methylaniline on benzil in the presence of alcohol and hydrochloric acid leads to the formation of *benzil-5-nitro-2-methylaminomonoanil*, yellow leaflets, m. p. 195°, 6-nitro-2:3-diphenylquinoxaline, 6-nitro-2:3-diphenyl-1-methylstilbazonium chloride, dark yellow needles, m. p. 168° (decomp.), and a substance, m. p. about 280°, which has not been completely investigated. More favourable conditions for the conversion of the anil into 6-nitro-2:3-diphenylquinoxaline and 6-nitro-2:3-diphenyl-1-methylstilbazonium chloride are described in detail. The  $\psi$ -base corresponding with the substance last mentioned crystallises in yellow needles, m. p. 170° (from alcohol), 176° (from benzene); repeated crystallisation from hot alcohol effects its re-conversion into the anil.

H. W.

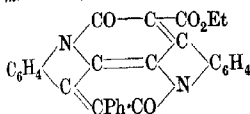
### The Indigotin Group. II. A New Vat Dye Prepared from Indigotin and Ethyl Malonate.

THEODOR POSNER and GOTTFRIED PYL (*Ber.*, 1923, 56, [B], 31–44; cf. Posner and Aschermann, A., 1920, i, 880).—A vat dye derived from indigotin and ethyl malonate has been patented by Posner (D.R.-P. 281998). The full investigation of the product is now described, the substance being of particular interest, since it gives violet-red shades which are quite distinct from the usual indigo colours.

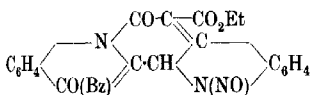
*Ethyl indigotinmalonate* (annexed formula), reddish-violet crystals, m. p. 296–297°, is prepared conveniently by heating a solution of indigotin in nitrobenzene with ethyl malonate and a little solid sodium hydroxide. It may also be obtained in poor yield by the protracted ebullition of a solution of indigotin in a large excess of ethyl malonate; as by-product of the latter action, a *carboxylic acid*,  $C_{18}H_{18}O_{10}$ , m. p. 129°, is formed which has not been investigated completely. It is converted by aqueous alcoholic



potassium hydroxide solution into the corresponding *potassium salt*,  $C_{21}H_{14}O_4N_2.KOH$ , an emerald-green powder. Hydrolysis of the carbethoxy group could not be effected by means of acid or alkali; the protracted action of the latter appears to cause the slow loss of the whole malonyl group without, however, giving a homogeneous product. The introduction of a second malonyl complex into ethyl indigotinmalonate could not be effected, but the compound reacts with phenylacetyl chloride in the presence of boiling xylene to yield *ethyl anhydrophenylacetylindigotinmalonate* (annexed formula), m. p. above  $310^\circ$ . *Ethyl benzoyldihydroindigotinmalonate*,  $C_{23}H_{20}O_5N_2$ , colourless leaflets which become red at about  $192^\circ$  and decompose without melting at a higher temperature, is prepared by reduction of ethyl indigotinmalonate with



sodium hyposulphite in the presence of sodium hydroxide and addition of benzoyl chloride to the solution. The presence of the imino-group in ethyl indigotinmalonate is established by the preparation of *ethyl benzoylindigotinmalonate*,  $C_{23}H_{18}O_5N_2$ , orange-coloured leaflets, m. p.  $240^\circ$ , which is obtained in small yield by boiling the ester and benzoyl chloride, or more conveniently from these substances in the presence of pyridine. Acetyl chloride and pyridine convert ethyl indigotinmalonate into *ethyl acetylindigotinmalonate*, red crystals, m. p.  $182^\circ$ . *Ethyl nitrosoindigotinmalonate*,  $C_{21}H_{13}O_5N_3$ , tile-red crystals, decomp.  $267-270^\circ$ , is prepared by the action of nitrous fumes on a boiling alcoholic suspension of ethyl indigotinmalonate, into which it is re-converted by successive treatment with zinc dust and air. It is not affected by a boiling mixture of acetic anhydride and acetyl chloride, but is converted by benzoyl chloride in the presence of boiling pyridine



into *ethyl benzoylnitrosoindigotinmalonate* (annexed formula), orange-yellow crystals which commence to sublime at  $236^\circ$  and

decompose at  $245-250^\circ$ ; it is hydrolysed by aqueous-alcoholic potassium hydroxide solution to ethyl nitrosoindigotinmalonate.

A compound,  $C_{21}H_{17}O_5N_3$ , small, almost colourless needles, which become red at  $210^\circ$ , is formed during the preparation of ethyl indigotinmalonate.

H. W.

**peri-Naphthindigotin.** SIKHIBHUSHAN DUTT (T., 1923, 123, 224-225).

**2:5-Iminodihydro-1:2:3-triazole. I. Constitution of Dimroth's 5-Anilinotriazole.** PAVITRA KUMAR DUTT (T., 1923, 123, 265-274).

**Purines. IV. The Action of Hydrogen Peroxide on certain Phenyl-substituted Uric Acids.** F. J. MOORE and ELIZABETH S. GATEWOOD (J. Amer. Chem. Soc., 1923, 45, 135-145).—It has

previously been shown (A., 1918, i, 104, 409, 410) that the action of hydrogen peroxide on uric acid may lead to two distinct series of products according to experimental conditions, but the results indicated no intermediate product between uric acid and the final products obtained. With a view to obtain information as to the relationship which may exist between the mechanism of this reaction and that of the permanganate oxidation, certain substituted uric acids have been prepared and their behaviour on oxidation by hydrogen peroxide has been studied.

9-Phenyluric acid on oxidation in alkaline solution with hydrogen peroxide gives *as*-phenylbiuret and a new phenylbiuret, m. p. 196—197.5° (cf. following abstract), together with ammonia, oxalic acid, and phenylcarbamide. 7-Methyluramil when treated in alkaline solution with phenylcarbamide yields 9-phenyl-7-methyl- $\psi$ -uric acid, m. p. 245—250°,  $n_D$  1.636;  $n_D$  1.714+, from which, by boiling with hydrochloric acid, 9-phenyl-7-methyluric acid,  $n_D$  1.887,  $n_D$  1.674, is obtained. On oxidation with hydrogen peroxide in the presence of potassium hydroxide, this uric acid gives oxalic acid, ammonia, and 6-phenyl- $\alpha$ -methylcarbamide. By a similar series of reactions starting with 1:3-dimethyluramil, 9-phenyl-1:3-dimethyl- $\psi$ -uric acid, m. p. 189—190°,  $n_D$  1.525,  $n_D$  1.647, giving a monohydrate, and 9-phenyl-1:3-dimethyluric acid,  $n_D$  1.155+,  $n_D$  1.684, are obtained. The latter compound, on oxidation as above, also yields ammonia, oxalic acid, and 6-phenyl- $\alpha$ -methylcarbamide.

9-Allyl- $\psi$ -uric acid, m. p. 227—228° (decomp.),  $n_D$  1.591,  $n_D$  1.69, is also obtained from the uramil and was converted into 9-allyluric acid,  $n_D$  1.75,  $n_D$  1.775. The optical properties of a number of familiar compounds allied to the above were determined during the work, and the results are tabulated.

From the above results on the oxidation of substituted uric acids, it is considered that the first step in the reaction is the breaking of the bonds between the carbon atoms 2 and 3, 4 and 5 and 5 and 7, forming in the case of 9-phenyluric acid *s*-phenylbiuret and in the cases of the other two the same phenylmethylbiuret. The phenylmethylbiuret then decomposes, giving ammonia, and phenylmethylcarbamide, while the *s*-phenylbiuret partly undergoes a similar decomposition, forming phenylcarbamide, and another portion is rearranged by the ammonia to form *as*-phenylbiuret.

W. G.

**Purines. V. A Third Phenylbiuret.** ELIZABETH S. GATEWOOD (*J. Amer. Chem. Soc.*, 1923, 45, 146—150; cf. preceding abstract).—The new phenylbiuret, m. p. 196—198° (decomp.),  $n_D$  1.559;  $n_D$  1.73, obtained during the oxidation of 9-phenyluric acid by hydrogen peroxide (*loc. cit.*) is clearly distinguished by its properties from the two isomerides already known. It can be converted into *as*-phenylbiuret by the action of ammonia and a great variety of organic bases, but not by alkalis. No method of reversing this change has been discovered. From certain theoretical considerations the author is inclined to the view that

the structure of this new biuret is that of *N*-phenylbiuret, a structure at present assigned by Schiff (A., 1907, i, 206) to the phenylbiuret prepared by Weith (A., 1878, 141). W. G.

**The Upper Limit of Diazotisability in the Benzene Series. Diazo-derivatives of Mesitylene.** GILBERT T. MORGAN and GLYN REES DAVIES (T., 1923, 123, 228—237).

**Azopicric Acid** [2:4:6:2':4':6'-Hexanitro-5:5'-dihydroxyazobenzene]. K. ELBS and FR. SCHLIEPHAKE (*J. pr. Chem.*, [ii], 1922, 104, 282—284).—The nitration of *m*-azophenol (cf. A., 1903, i, 539) by the prolonged action of an ice-cold mixture of concentrated sulphuric acid and potassium nitrate, subsequent treatment with water, and extraction with benzene, leads to the compound of 1 mol. of azopicric acid with 2 mols. of benzene, flat, deep blood-red prisms; this loses benzene gradually, more quickly on warming at 90°, giving a 60% yield of pure *azopicric acid* as a yellowish-red powder, m. p. 238—239° (decomp.), which explodes violently when quickly heated. Azopicric acid dissolves readily in benzene (giving the above-mentioned compound), and also in water, alcohol, ether, or acetone, but is insoluble in carbon disulphide or concentrated hydrochloric acid. In aqueous solution it is a fast dye to wool, and has an astringent (not bitter) taste. The potassium and barium salts are described. W. S. N.

**Capacity to Form Phenylhydrazones.** VI. BERNARDO ODDO and LUIGI PIATTI (*Gazzetta*, 1922, 52, ii, 333—346).—Cryoscopic investigations in anhydrous phenylhydrazine, similar to those already described (A., 1913, i, 1233; 1915, ii, 414, 415), have now been made on a number of compounds containing in the molecule either two carbonyl groups or one carbonyl together with other radicles.

Diacetyl reacts immediately with the phenylhydrazine, giving a precipitate which does not dissolve readily. After a time, however, the liquid becomes almost clear, and the depression of the freezing point gradually attains a value which is 50% of the theoretical value for the diacetyl taken, the formation of the monophenylhydrazone being thus indicated. Later, the phenylosazone is precipitated in increasing amount. Similar difficulties as regards solubility are presented by anthraquinone, with which a clear solution cannot be obtained.

With acetylacetone, the apparent molecular weight rapidly reaches a value equal to 40% of the theoretical value, and subsequently slowly falls to become constant at about one-third the calculated value, the diphenylhydrazone or, more probably, the pyrazole compound being formed:  $\text{OH}\cdot\text{CMe}\cdot\text{CHAc} + \text{NH}_2\cdot\text{NPh} = \text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{N}\cdot\text{NPh} + \text{H}_2\text{O} = \begin{matrix} \text{N}=\text{CMe} \\ \text{NPh}\cdot\text{CMe} \end{matrix} \text{CH} + 2\text{H}_2\text{O}$ . Similar

results are obtained with benzil, except that the initial velocity of the reaction is somewhat less. With dipyrrolyl, although the phenylosazone is known, no reaction with phenylhydrazone occurs under the experimental conditions of the present investigation.

As regards terpenic ketones, camphor, bromocamphor, and

fenchone, which are bicyclic, are inert towards phenylhydrazine. The monocyclic pulegone, however, reacts completely, the molecular weight falling at approximately constant velocity to about 60% and then at gradually diminishing velocity to 52% of the theoretical value. Menthone behaves similarly to pulegone, with which, rather than with the other terpenic ketones examined, it presents structural analogies. Carvone is inactive towards phenylhydrazine, the double linking in the nucleus possibly favouring an enolic configuration. Santonin also is inactive.

The results obtained with aldehydes emphasise the promptitude with which the aldehydic function is exercised in presence of phenylhydrazine. The aldehydes investigated were dextrose, cuminaldehyde (isopropylbenzaldehyde), *o*-, *m*-, and *p*-nitrobenzaldehydes, phenylacetaldehyde, cinnamaldehyde, *m*-nitrocinnamaldehyde, vanillin, *p*-dimethylaminobenzaldehyde, furfuraldehyde, and phthalaldehyde. None of these remains inert towards phenylhydrazine, and most of them quickly precipitate the phenylhydrazones. Furfuraldehyde reacts instantly, but gives no precipitate. With phenylacetaldehyde, which also yields no precipitate, the reaction is somewhat slow in its final phase, this thus resembling the aliphatic aldehydes. Cinnamaldehyde and its *m*-nitro-derivative, on the other hand, exhibit towards phenylhydrazine the behaviour of an aromatic aldehyde, in spite of the fact that the aldehyde group lies in the side chain.

Dextrose furnishes no precipitate with phenylhydrazine, but the reaction proceeds with the regularity shown in the case of the aliphatic aldehydes, although the retarding influence of the alcoholic groups is manifest. Phthalaldehyde behaves abnormally, the value of the molecular weight in phenylhydrazine solution being only 23% of the value calculated from the amount of the aldehyde taken.

T. H. P.

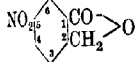
**The Opening of the Lactone Ring of Phthalide Derivatives by Hydrazine.** J. TEPPEMA (*Rec. trav. chim.*, 1923, 42, 30-68).—The object of this work was to study the influence on the stability of the lactone ring in phthalide of substituents both in the benzene ring and in the methylene group of the lactone ring. The stability of the ring is gauged by the ability or otherwise of hydrazine to open the ring with formation of a benzhydrazide and further by the stability of aldehydo- and keto-derivatives of the benzhydrazide. The action of hydrazine on phthalide was studied by Wedel, who concluded that the product formed was the hydrazide of *o*-hydroxymethylbenzoic acid (A., 1900, i, 363), but Blaise and Luttringer concluded that the additive compound was formed at the keto-group without rupture of the lactone ring (A., 1905, i, 329). The results of the present work do not support the latter view. A number of derivatives of *o*-hydroxymethylbenzhydrazide with aldehydes and ketones were prepared.

*p*-Methoxybenzylidene-*o*-hydroxymethylbenzhydrazide,  
 $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe},$

forms colourless needles, m. p. 165°. *iso*Propylidene-*o*-hydroxy-

*methylenbenzhydrazide* forms colourless spangles, m. p. 148°. A derivative could not be obtained with acetophenone. *d-Mannose-o-hydroxymethylbenzhydrazide* crystallises in colourless needles, m. p. 106–109°; in boiling aqueous solution it is decomposed by benzaldehyde with formation of benzylidene-*o*-hydroxymethylbenzhydrazide. *d-Galactose-o-hydroxymethylbenzhydrazide* was obtained in crystals, m. p. 70–75°, but could not be recrystallised unchanged. The corresponding dextrose derivative was obtained only as a syrup; it is decomposed by benzaldehyde in hot aqueous solution. An acetyl derivative of *o*-hydroxymethylbenzhydrazide can be obtained by the action of acetic anhydride in the cold. Its decomposition in the hot, with formation of phthalide, accounts for Wedel's failure to prepare it. The acetyl compound does not react with benzaldehyde and must therefore be a *N*-acetyl derivative. *N-Acetyl-o-hydroxymethylbenzhydrazide*,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NHAc}$ , forms colourless spangles, m. p. 146°. No benzoyl derivative of *o*-hydroxymethylbenzhydrazide could be obtained with benzoyl chloride.

The mono-nitro-derivative obtained by nitrating phthalide either with pure nitric acid or with a nitrate and sulphuric acid is 5-nitrophthalide, m. p. 143°, not 4-nitrophthalide as stated by Hoenig (A., 1886, 242). In the literature different methods of notation are adopted by different authors; the present author adopts the method shown in the annexed formula. 5-Nitro-2-hydroxymethylbenzhydrazide forms yellow needles, m. p. 167–168°. The isopropylidene derivative of this forms colourless needles, m. p. 165°; the benzylidene derivative forms colourless spangles, m. p. 167°.



The aldehyde and ketone derivatives of nitro-*o*-hydroxymethylbenzhydrazide are not hydrolysed so readily as those of *o*-hydroxymethylbenzhydrazide, with re-formation of the phthalide, and, conversely, the presence of the nitro-group facilitates the rupture of the lactone ring. *N-Acetyl-5-nitro-2-hydroxymethylbenzhydrazide* forms colourless spangles, m. p. 171°; when boiled with acetic anhydride, it is decomposed, forming 5-nitrophthalide.

5-Aminophthalide is best prepared by reducing 5-nitrophthalide with hydrogen sulphide in ammoniacal alcoholic solution. When reduced with phosphorus and hydrogen iodide, it gives an amino-*o*-toluic acid, m. p. 196°, not 153°, as stated by Hoenig. This was identified as 4-amino-*o*-toluic acid, which establishes the constitution of the above 5-nitrophthalide. 4-Amino-*o*-toluic acid was synthesised by a new method, through the steps 4-nitro-*o*-toluidine,  $\rightarrow$  4-nitro-2-cyanotoluene  $\rightarrow$  4-amino-2-cyanotoluene  $\rightarrow$  4-amino-*o*-toluic acid.

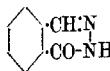
The lactone ring of 5-aminophthalide is opened by hydrazine with formation of 5-amino-2-hydroxymethylbenzhydrazide, colourless needles, m. p. 147°; benzylidene derivative, m. p. 161°; isopropylidene derivative, m. p. 170°. 5-Acetamidophthalide forms colourless needles, m. p. 222–223°. When 5-amino-2-hydroxymethylbenzhydrazide is treated with cold acetic anhydride, it forms the diacetyl derivative, 5-acetamido-2-hydroxymethylacetylbenzhydrazide,

small colourless needles, m. p. 195°; but with hot acetic anhydride, 5-acetamidophthalide is formed.

Contrary to the statement of Hoenig, 5-aminophthalide can be readily diazotised and transformed almost quantitatively into a halogen derivative by Sandmeyer's method. 5-Chlorophthalide forms colourless needles, m. p. 110°; 5-bromophthalide forms similar crystals, m. p. 98°. 5-Chloro-2-hydroxymethylbenzhydrazide forms colourless needles, m. p. 139°; benzylidene derivative, m. p. 165—166°; isopropylidene derivative, m. p. 153°; acetyl derivative, m. p. 160°. 5-Bromo-2-hydroxymethylbenzhydrazide forms colourless needles, m. p. 152°; benzylidene derivative, m. p. 171°; isopropylidene derivative, m. p. 157°; acetyl derivative, m. p. 153°.

The introduction of a single methyl, ethyl, or phenyl group into phthalide in the  $\alpha$ -position stabilises the lactone ring to such an extent that hydrazine cannot effect the rupture. A chloro-, bromo-, or nitro-group in the 5-position of  $\alpha$ -methylphthalide weakens the lactone ring sufficiently to permit rupture by hydrazine, but this is not the case with  $\alpha$ -ethylphthalide or  $\alpha$ -phenylphthalide. 5-Amino- $\alpha$ -ethyl- and 5-amino- $\alpha$ -methyl-phthalide do not react with hydrazine. The dialkyl and diphenylphthalides are extremely stable and their inactivity towards hydrazine is not affected by substituents in the 5-position.

$\alpha$ -Methylphthalide has  $n_D^{20}$  1.5450,  $d_4^{20}$  1.1601, m. p. 7°. 5-Nitro- $\alpha$ -methylphthalide, the principal nitration product of  $\alpha$ -methylphthalide, is accompanied by a small quantity of an isomeride, probably the 3-nitro-compound. With hydrazine, 5-nitro- $\alpha$ -methylphthalide gives 5-nitro-2- $\alpha$ -hydroxyethylbenzhydrazide,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , forming colourless needles, m. p. 120°. The isopropylidene derivative has m. p. 127°, but when recrystallised from alcohol partly decomposes with regeneration of the lactone. A benzylidene derivative could not be obtained on account of the formation of lactone. The lactone ring in 5-nitro- $\alpha$ -methylphthalide is therefore more stable than that in 5-nitrophthalide. 5-Nitro-2- $\alpha$ -hydroxyethyl-acetylbenzhydrazide, m. p. 126°, has similar properties to the other acetyl derivatives described. 5-Amino- $\alpha$ -methylphthalide does not react with hydrazine. From it were prepared 5-chloro- $\alpha$ -methylphthalide, colourless needles, m. p. 45°, and 5-bromo- $\alpha$ -methylphthalide, m. p. 59°. 5-Chloro-2- $\alpha$ -hydroxyethylbenzhydrazide forms colourless needles, m. p. 108°; its isopropylidene derivative has m. p. 119°. The 5-bromo-2- $\alpha$ -hydroxyethylbenzhydrazide has m. p. 119° and its isopropylidene derivative 135°. 5-Amino- $\alpha$ -ethylphthalide was obtained by reduction of the corresponding nitro-compound; it forms small, yellow needles, m. p. 140°. From this were obtained 5-chloro- $\alpha$ -ethylphthalide, colourless needles, m. p. 54°, and 5-bromo- $\alpha$ -ethylphthalide, similar crystals, m. p. 63°. By the action of hydrazine on  $\alpha$ -amino- or  $\alpha$ -bromo-phthalide, 1-keto-1:2-dihydrophthalazine (annexed formula) is obtained, and the same substance is formed from hydrazine and diphtalide ether, which thus behaves as the anhydride of phthalaldehydic acid. 5-Amino- $\alpha$ -dimethylphthalide cry-



tallises in colourless needles, m. p. 115°. With bromine, it gives 4:6-dibromo-5-amino- $\alpha$ -dimethylphthalide, colourless needles, m. p. 138°. 4:6-Dibromo-5-amino- $\alpha$ -diethylphthalide crystallises in spangles, m. p. 93°. Not one of these derivatives of a dialkylphthalide is acted on by hydrazine. The work serves to confirm and extend Hjelt's rule regarding the stability of lactone rings (A., 1891, 822).  
E. H. R.

**The Configuration of the Doubly-linked Tervalent Nitrogen Atom. The Resolution of the Pyridylhydrazones of cyclo-Hexylene Dithiocarbonate.** WILLIAM HOBSON MILLS and HANS SCHINDLER (T., 1923, 123, 312—323).

**The Ionisation of Protein Chlorides.** DAVID I. HITCHCOCK (J. Gen. Physiol., 1923, 5, 383—394).—By the use of the silver-silver chloride electrode and the hydrogen electrode, electrometric determinations have been made of the chloride and hydrogen-ion concentrations in solutions of proteins (gelatin, egg-albumin, casein, edestin, and serum-globulin) to which varying quantities of hydrochloric acid have been added. It is concluded that the hydrochlorides of these proteins are strongly ionised, and that there is no marked repression of the ionisation by excess of hydrochloric acid.  
W. O. K.

**Density of Albumin Solutions.** M. A. RAKUSIN and G. D. FLEISHER (Chem. Ztg., 1923, 47, 66).—A table is given of the density of albumin solutions at 17° up to a concentration of 15.35%, at which the solution is saturated. White of egg is a saturated solution of albumin. When freed from fat and clarified by treatment with lead acetate, albumin has a considerably lower density than the crude substance, the value for a 5% solution being  $d_{15}^{15}$  1.01288 for the pure substance and  $d_{15}^{15}$  1.01341 for the crude. The specific rotatory power is unchanged by the purifying process.  
H. C. R.

**The Nature of Nucleins.** S. NAKAGAWA (Z. physiol. Chem., 1923, 124, 274—277).—Hydrolysis of nucleoprotein by pepsin yields no nuclein. The idea of Steudel is confirmed that nucleoproteins are loose compounds of nucleic acid and a protein base.  
W. O. K.

**The Hydrolysis of Proteins by Strong Sulphuric Acid.** E. SALKOWSKI (Biochem. Z., 1922, 133, 1—20).—Horn, on complete hydrolysis by three times its weight of 73.6% sulphuric acid, gives practically no humin material. The hydrolysate reduces Fehling's solution to an extent which indicates the presence of 13% of apparent sugar. Pyruvic acid, aldehydes of the aliphatic series, and furfuraldehyde are also present.  
W. O. K.

**Heteroalbumose.** E. ZUNZ and P. GYÖRGY (Bull. Acad. roy. Belg., 1914, 359—380).—An investigation of Pick's heteroalbumose (A., 1900, i, 68) by two methods: (1) Fractionation by Siegfried's method (A., 1906, i, 144) and (2) ultra-filtration, using collodion and acetic acid of three different concentrations. The authors

conclude that Pick's hetero-albumose is really a mixture. The chief constituent (insoluble in twice its bulk of 95% alcohol) is a heteroalbumose with  $[\alpha]_D^{25} -72.5^\circ$ , but associated with it are several protoalbumoses of low rotatory power and soluble in twice their bulk of alcohol. One of these is apparently responsible for the Adamkiewicz reaction given by some preparations of Pick's heteroalbumose. Altogether, fifteen different fractions of the latter are examined and compared with the original substance by means of elementary analysis, rotatory power, gold numbers, refractive indices, etc. E. E. T.

**Bioluminescence. XV. Electro-reduction of Oxy-luciferin.** E. NEWTON HARVEY (*J. Gen. Physiol.*, 1923, 5, 275-284).—If a solution containing luciferin and luciferase and some sodium chloride is electrolysed, the oxy-luciferin is reduced at the cathode by the nascent hydrogen, and as it is oxidised back again in the presence of the luciferase, by the oxygen dissolved in the water, with the production of light, there is immediately luminescence. Similar reduction by nascent hydrogen also takes place at the surface of metals (aluminium, manganese, zinc, and cadmium) when these are immersed in water containing oxy-luciferin, although there is no actual production of molecular hydrogen. Other systems are described where electrochemical reduction of luciferin occurs. In general, the production of light by the combination oxy-luciferin-luciferase is a very good test for nascent hydrogen. Molecular hydrogen does not produce luminescence. If, however, a palladiumised surface be introduced, it becomes strongly luminescent, as it activates the hydrogen. W. O. K.

**The Mechanism of the Effect of Acids and Alkalis on the Digestion of Proteins by Pepsin or Trypsin. A Correction.** JOHN H. NORTHROP (*J. Gen. Physiol.*, 1923, 5, 415; cf. this vol., i, 69).—A statement made in the previous paper (*loc. cit.*) to the effect that the amount of acid required to bring protein solution to a given  $P_H$  is independent of the nature and valency of the anion is true only of strong acids. W. O. K.

**Influence of Reaction on the Activity of Trypsin. II.** W. E. RINGER (*Z. physiol. Chem.*, 1923, 124, 171-193; cf. A., 1922, i, 282).—The solution of fibrin by trypsin is inhibited by sulphates, thiocyanates, and ferrocyanides, but more strongly by multivalent cations such as calcium, which also strongly inhibit the swelling of fibrin in water. The effects, however, are not quite analogous; bile salts, for example, completely inhibit the solution of fibrin at concentrations at which the effect on the swelling is quite inappreciable. Salts with multivalent cations affect the viscosity of alkaline protein solutions (dialysed serum). The effect of these salts on the tryptic hydrolysis of such solutions is at first one of inhibition, but this very soon disappears. Experiments confirm the fact that alkaline protein solutions show a gradual increase in internal friction and that after a long time the internal friction again becomes less. W. O. K.

**Equilibrium between the so-called "Antitrypsin" of the Blood and Trypsin.** RAYMOND G. HUSSEY and JOHN H. NORTROP (*J. Gen. Physiol.*, 1923, 5, 335—351).—From a study of the inhibition of trypsin by blood plasma, it is concluded that the effect is not one of adsorption, but that it is more probably chemical in nature. It is shown that if the assumption is made that an easily dissociated compound of the trypsin and the inhibiting substance is formed, the law of mass action is obeyed according to the equation  $[\text{Trypsin}][\text{inhibiting substance}]/[\text{Compound of Trypsin and inhibiting substance}] = K$ . Equilibrium is attained very quickly and is reversible, and this fact opposes the view that there is an adsorption. Quantitative experiments have been carried out by the authors' method on (1) the effect of adding varying amounts of plasma to a constant amount of trypsin, (2) the effect of adding varying amounts of trypsin to a constant amount of plasma, and (3) the effect of dilution on a plasma-trypsin mixture, and the results accord with the theory that a reversible equilibrium is attained. These conclusions are in harmony with the results that have been obtained with other enzymes.

W. O. K.

**Invertase.** A. FODOR (*Z. physiol. Chem.*, 1923, 124, 278—281).—Criticism of the results of Willstätter, Graser, and Kuhn (A., 1922, i, 1200), pointing out the difficulty of being certain of the purity of the preparations obtained.

W. O. K.

**Kinetic Researches on Saccharase.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 124, 159—170).—The unimolecular reaction constant  $k$  is determined for the inversion of sucrose by saccharase (invertase), from the expression  $k = 1/t \cdot \log a/(a-x)$ , where  $x$  is the amount of sucrose inverted in a time  $t$  out of the initial amount  $a$ . With increasing values of  $c$ , the initial concentration of the sucrose, the value of the product  $kc$  increases until  $c$  is about 4 g. per 100 c.c., after which it is constant until  $c$  is about 20 g. per 100 c.c., and then it decreases. If, on the assumption that a reversible equilibrium is reached between enzyme and substrate, the constant  $K = [\text{Enzyme}][\text{Substrate}]/[\text{Enzyme Substrate}]$  is calculated, which is possible if it be also assumed that all the enzyme is combined with the substrate when  $k$  is maximal, it is found to vary from 0.027 to 0.0175.

W. O. K.

**Influence of Amino-acid in Protecting Amylase from Inactivation by Mercury.** H. C. SHERMAN and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1922, 44, 2923—2926).—Glycine and phenylalanine and presumably other amino-acids protect against small concentrations of mercuric chloride added when testing the activity of purified pancreatic amylase and allow the latter to act almost as efficiently as if no mercury were present. The minute amounts of mercury which might conceivably have been present in the histidine and tryptophan preparations used could not, therefore, account for their entire lack of activating influence on

the amylolytic action of the enzyme as previously recorded (A., 1922, i, 283). W. G.

**Influence of Lysine on the Hydrolysis of Starch by Purified Pancreatic Amylase.** H. C. SHERMAN and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1922, 44, 2926—2930).—Lysine has no effect on the amylolytic action of pancreatic amylase, but exerts a favourable influence on its saccharogenic action. Accepting the view that the enzyme (pancreatic amylase) is essentially a protein substance which gradually becomes inactivated through hydrolysis in the aqueous medium in which it acts, and that the apparent activating influence of amino-acids is due to retardation of this hydrolysis of the enzyme, it is suggested that the lysine in the enzyme molecule is not split off until after the stage of amylolytic action has passed, but is only concerned in the later stages represented by saccharogenic activity. These observations confirm and extend the theory advanced to explain the effect of histidine and tryptophan on the same enzyme (A., 1922, i, 283). W. G.

**Influence of some Organic Compounds upon the Hydrolysis of Starch by Salivary and Pancreatic Amylases.** H. C. SHERMAN and NELLIE M. NAYLOR (*J. Amer. Chem. Soc.*, 1922, 44, 2957—2966).—The authors consider that the favourable effect reported by Rockwood (A., 1917, i, 358; 1918, i, 86, 274) to be exerted by several types of organic compounds on the activity of amylolytic enzymes was due in most, if not in all, cases, other than those of natural amino-acids, to hydrogen-ion or salt effects, rather than to the organic structure of the compounds. In the presence of favourable concentrations of chloride-, phosphate-, and hydrogen-ions, no favourable effect on the activity of the enzyme was shown by methyl- and ethyl-amine hydrochlorides, aniline sulphate, benzoic acid, benzamide, anthranilic acid, or hippuric acid. Previous results as to the favourable influence of several amino-acids resulting from protein hydrolysis have been confirmed and extended. This influence may be attributed either to a direct activating effect dependent on the structural nature of these substances as  $\alpha$ -amino-acids or to conservation of the enzyme by retarding its hydrolysis, but the results with hippuric acid fail to confirm the activation hypothesis. W. G.

**Some Actions of Thorium-X on Diastases and Micro-organisms.** J. P. AVERSENQ, L. JALOUSTRE, and E. MAURIN (*Compt. rend.*, 1923, 176, 193—195).—Thorium-X, at the concentrations used, activates in a marked manner the hydrolysing and oxidising enzymes studied, the increased action in a given time being of the order of 30%. Similarly, relatively small amounts of thorium-X were capable of increasing the vitality of certain pathogenic organisms and of certain living cells. W. G.

**Peroxydase.** III. RICHARD WILLSTÄTTER and ADOLF POL-LINGER (*Annalen*, 1923, 430, 269—319).—In continuation of previous work (A., 1918, i, 555) on the purification of peroxydase

preparations, the authors have made a detailed study of the influence of adsorption on and subsequent elution from alumina and kaolin, and of precipitation by tannic acid, on the activity of peroxydase solutions. On the basis of these experiments, two methods of purification are worked out in detail, the results of each operation being followed by determinations of the "purpurogallin number" (*loc. cit.*). According to one method, the peroxydase in a solution having a purpurogallin number 302 is first adsorbed on alumina suspended in 50% alcohol, removed in carbonic acid solution, and then again adsorbed on alumina in dilute alcohol. One further adsorption on kaolin in 50% alcohol and three subsequent adsorptions on alumina raise the purpurogallin number to 1900, the highest value as yet observed. According to the second method, the peroxydase is subjected to four adsorptions on alumina in 50% alcohol and three on kaolin in 0.02N-acetic acid, and a precipitation by tannin, the final purpurogallin number being 3070.

The question as to whether iron enters into the constitution of peroxydase cannot be conclusively settled on the analytical data, because, although for a given natural source and method of purification the iron content runs roughly parallel with the purpurogallin number, a change either in the source or the process affects the proportion of iron in a way which cannot at present be simply accounted for.

C. K. I.

**Reductases. II. Comparison of the Influence of Alkalis on Potato Reductase.** I. A. SMORODINCEV (*Z. physiol. Chem.*, 1923, 124, 202—210; cf. A., 1922, i, 1201).—The effect of alkali on the reductase in potatoes (nitrase) is to inhibit the activity, an effect apparently independent of the kation, and due to the hydroxyl-ion concentration.

W. O. K.

**Mode of Action of Vitamins.** ANTONIO DE GREGORIO ROCASOLANO (*Anal. Fis. Quim.*, 1922, 20, 433—436).—Theoretical. The vitamins are held to act as colloidal catalysts.

G. W. R.

**Vitamins-B and -D.** CASIMIR FUNK and JULIA B. PATON (*J. Metabolic Research*, 1922, 1, 737—775).—Vitamin-B is destroyed by alkali and also by heating in an autoclave under pressure for three hours; the effect of such treatment on vitamin-D is much smaller. When grown in a solution containing both vitamins, yeast or other fungi removes the latter, which is retained tenaciously by the yeast-cells.

CHEMICAL ABSTRACTS.

**An Attempt to Resolve Quaternary Phosphonium Compounds.** L. G. RADCLIFFE and W. H. BRINDLEY (*Chemistry and Industry*, 1922, 42, 64—66).—In the hope of effecting a resolution of a quaternary phosphonium compound, *phenyl-p-tolylmethyl-allylphosphonium d-bromocamphorsulphonate* was prepared, but attempts to crystallise it failed; it was only obtained as a jelly-like mass, finally becoming resinous. The synthesis of the compound was accomplished from *p*-tolylidichlorophosphine, through *phenyl-p-tolylchlorophosphine* to *phenyl-p-tolylmethylphosphine*,

which was then combined with allyl iodide. The final yield was very small. Attempts to prepare phenyl-*p*-tolylethyl-*n*-butylphosphonium iodide from phenyl-*p*-tolylethylphosphine and *n*-butyl iodide led only to the formation of an uncrystallisable oil.

E. H. R.

**Additive Reactions of Phosphorus Halides. VI. The 1:2- and 1:4-Addition of Diphenylchlorophosphine.** J. B. CONANT, J. B. S. BRAVERMAN, and R. E. HUSSEY (*J. Amer. Chem. Soc.*, 1923, **45**, 165—171; cf. A., 1921, i, 69).—Diphenylchlorophosphine reacts with benzaldehyde and phenyl styryl ketone in the presence of glacial acetic acid, giving, respectively, an hydroxy- and a keto-phosphine oxide. By using acetic anhydride in place of the acid, the mechanism of the reaction with the unsaturated ketone has been established. Under these conditions, an un-

saturated intermediate compound,  $O(PPh_2 \begin{smallmatrix} \diagup O-CPh \\ \diagdown CHPh \end{smallmatrix} \diagup CH)_2$ , is formed, but could not be isolated in a crystalline state. On treatment with water, it gives the ketophosphine oxide, and it readily combines with two equivalents of bromine to yield a dibromide without the evolution of hydrogen bromide. This dibromide, not isolated as such, on treatment with water gives a mixture of two isomeric monobromoketophosphine oxides, one of which can be obtained by direct bromination of the ketophosphine oxide itself. These two monobromo-derivatives behave differently towards alcoholic sodium hydroxide. The one with the high m. p. loses hydrogen bromide to give an unsaturated ketophosphine oxide, whilst the other is reduced to the ketophosphine oxide. On the other hand, by boiling it with potassium acetate in methyl alcohol, the bromo-compound with the high m. p. is reduced to the ketophosphine oxide.

The following compounds are described. *Diphenyl- $\alpha$ -hydroxybenzylphosphine oxide*, m. p. 230°, obtained from benzaldehyde and diphenylchlorophosphine. *Diphenyl- $\beta$ -benzoyl- $\alpha$ -phenylethylphosphine oxide*, m. p. 227°, similarly obtained from phenyl styryl ketone. *Diphenyl- $\beta$ -*p*-chlorobenzoyl- $\alpha$ -phenylethylphosphine oxide*, m. p. 225—226°. *Diphenyl- $\beta$ -bromo- $\beta$ -benzoyl- $\alpha$ -phenylethylphosphine oxide*, in two isomeric forms, m. p. 187° and 158°, respectively. *Diphenyl- $\beta$ -bromo- $\beta$ -*p*-chlorobenzoyl- $\alpha$ -phenylethylphosphine oxide*, in two isomeric forms, m. p. 196° and 187°, respectively. *Diphenyl- $\beta$ -benzoyl- $\alpha$ -phenylvinylphosphine oxide*, m. p. 143°; and *diphenyl- $\beta$ -*p*-chlorobenzoyl- $\alpha$ -phenylvinylphosphine oxide*, m. p. 151°.

W. G.

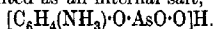
**Tetraphenyldiarsine.** PARRY BORGSTROM and MARGARET M. DEWAR (*J. Amer. Chem. Soc.*, 1922, **44**, 2915—2923).—An extension of previous work (A., 1920, i, 196). When tetraphenyldiarsine is prepared in a pure state, out of contact with air, its m. p. is 130—130.5° (corr.) (cf. Michaelis and Schulte, A., 1883, 187). Quantitative data are given for its oxidation in moist air and for its absorption of iodine, which latter decreases with the

age of the solution. This decrease in iodine absorption corresponds with an increase in molecular weight as determined cryoscopically in naphthalene as solvent. The specific conductivity in liquid sulphur dioxide increases with the age of the solution, changing from  $13.3 \times 10^{-6}$  to  $100 \times 10^{-6}$  mhos in nineteen days. The conductivity also increases with rise in temperature. The data indicate that the bond between the arsenic atoms of the tetraphenyldiarsine is easily broken. Bivalent arsenic of the type  $\text{Ph}_2\text{As}$  may be present transitorily in solution, but it is doubtful if it is the stable form. The valency or configuration of the stable form is not known.

Tetraphenyldiarsine reacts with methyl iodide, forming dimethyldiphenylarsonium iodide (cf. Steinkopf and Schwen, A., 1921, i, 694).  
W. G.

**Some Determinations of Molecular Weight in the Arsinic Acid Series.** RICHARD LORENZ and ELISABETH BREEHER (*Ber.*, 1923, 56, [B], 174—176; cf. Lorenz and Schmidt, A., 1920, i, 777, 897; ii, 465).—The molecular weights of arsanilic, *o*-toluidino-, resorcinic-, 3-nitro-4-aminophenyl-, 3-nitro-4-hydroxyphenyl-, 3-nitrophenyl-, *p*-phenylenedi-, and *o*-phenylenediamine-arsinic acids have been estimated in aqueous solution by the ebullioscopic method. They appear generally to have the simple, non-polymerised structure of the type  $\left[ \text{Ph} \cdot \text{AsO} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} \right]_{\text{H}}$ . *o*-Phenylenediaminearsinic acid, however, is polymerised to such an extent that it may exhibit double the normal molecular weight, but different preparations give different values.

Arsanilic acid,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_2)_2\text{H}_2$ , is strictly monobasic, and is preferably represented as an internal salt,



Similar observations are recorded with *o*-toluidinoarsinic acid, *p*-dimethylaminophenylarsinic acid, and *o*-phenylenediaminearsinic acid. Resorcinic-, 3-nitro-4-aminophenyl-, dichlorophenyl-, dibromophenyl-, 3-nitro-4-hydroxyphenyl-, *p*-iodophenyl-arsinic acids, and 4-amino-3-carboxyphenyl-arsine oxide behave normally with regard to electrical conductivity and exhibit normal molecular weights.  
H. W.

**Preparation of Mercury Dibenzyl.** A. GARCIA BANÚS (*Anal. Fis. Quím.*, 1922, 20, 667—668).—Mercury dibenzyl is prepared by treating benzyl chloride with excess of magnesium dust and adding mercuric chloride to the liquid, after decanting from excess of magnesium. The mixture is heated with frequent shaking under a reflux apparatus. Dilute acetic acid is added, and mercury dibenzyl is obtained by crystallisation from the ethereal solution. It has m. p. 110—111°.  
G. W. R.

### Physiological Chemistry.

**The Importance of Amides in Plant Feeding-stuffs.** F. HONCAMP (*Z. angew. Chem.*, 1923, 36, 45—49).—It is shown that urea may, at least partly, replace protein in feeding-stuffs without any injury to the animal. A. G. P.

**The Possibility of Urea as a Source of Protein in Ruminants. The Excretory Function of the Skin.** ARTHUR SCHEUNERT, WILHELM KLEIN, and MARIA STEUBER (*Biochem. Z.*, 1922, 133, 137—191).—From experiments in which urea was administered to animals as the source of nitrogen, it has been found impossible to demonstrate that it can function as a source of protein. W. O. K.

**The Measurement of Buffering.** GÜNTHER LEHMANN (*Biochem. Z.*, 1922, 133, 30—45).—A valuable measure of the buffering of a solution is given by  $b/(P_{H_1}-P_{H_2})$  where  $P_{H_1}$  is measured before and  $P_{H_2}$  after the addition to 10 c.c. of the buffer solution of a small quantity  $b$  of hydrochloric acid (or sodium hydroxide) measured in c.c. of 0.01N-solution. The  $P_H$  values are conveniently determined colorimetrically. Examples are given, chiefly of liquids of physiological importance. Values above 8 indicate strong buffering, 0.5—4, weak buffering, and below 0.5 no buffering. Blood gives a value of about 11. W. O. K.

**Comparative Buffering Value of American Peptones.** J. BRONFENBRENNER, G. G. DE BORD, and P. F. ORR (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 16).—The  $p_H$  of the various peptone solutions was determined electrometrically before and after the addition of measured amounts of acid and alkali, respectively. The initial reactions of the different solutions varied greatly; so did their buffer actions at a given  $p_H$ , some being 5 times greater than others. The buffering effect varied at different zones of  $p_H$ , being most marked between  $p_H$  9 and 8, and least between  $p_H$  5 and 4. For a given peptone the buffering varied at different  $p_H$  zones; the absolute concentration of buffer salts was highest at the lowest  $p_H$  and not at neutrality or high  $p_H$  as would be most desirable in media for use in the identification of bacteria by cultural methods. CHEMICAL ABSTRACTS.

**Antiketogenesis.** A. I. RINGER (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 97—99).—Glyceraldehyde, dihydroxyacetone, pyruvaldehyde, and pyruvic and lactic acids, when fed to diabetic animals, are completely and directly converted into dextrose and excreted in the urine, whilst acetaldehyde and possibly ethyl alcohol possess antiketogenetic properties. CHEMICAL ABSTRACTS.

**Chemical Researches on Nuclear Staining.** H. STEUDEL and SHUNGO OSATO (*Z. physiol. Chem.*, 1923, 124, 227—246).—It is considered probable that, in nuclear staining, a chemical

reaction takes place of the type: clupein nucleate+hydrochloride of the dye  $\rightarrow$  nucleate of the dye+clupein hydrochloride. By measuring the crystal violet absorbed from solutions of various strengths by heads of spermatozoa, it is shown that, if this assumption be true, the reaction does not proceed to completion, but that probably an equilibrium is set up. Similar results are obtained with protamine nucleic acid, with the nuclei of goose erythrocytes, with thymus leucocytes, and with nucleohiston, and also with other dyes—methylene-blue and eosin. W. O. K.

**The Nitrogenous Compounds Extracted from Testicles of the Ox.** KIYOSHI MORINAKA (*Z. physiol. Chem.*, 1923, 124, 259—266).—In an extract of ox testicles the following compounds have been identified: creatine, adenine, xanthine, arginine, histidine, choline, inositol, and probably guanine and hypoxanthine. W. O. K.

**The Maximal Quantity of the Glycogen Reserve in the Livers of Dogs of Different Ages.** (MMR) Z. GRUZEWSKA and E. FAURÉ-FRÉMIET (*Compt. rend.*, 1922, 175, 1237—1240; cf. A., 1921, i, 699).—Dogs were fed on a special diet and the liver and muscles analysed in order to determine the time during which the accumulated reserve of glycogen could remain unused in the liver. The conclusions are drawn that prolonged over-feeding was only tolerated by the liver in the case of a young and vigorous animal, and that the glycogenic function of the hepatic cell undergoes some modification either with age or with unfavourable circumstances without any apparent change in histological aspect. Further, in order to find the maximum glycogen content in the liver of a dog kept on an appropriate diet, the analysis must be carried out before the animal has attained its original weight as measured before fasting. H. J. E.

**Auto-oxidation and Anti-oxygen Action.** IV. CHARLES MOUREU and CHARLES DUFRAISSE (*Anal. Fis. Quim.*, 1922, 20, 383—393; cf. A., 1922, i, 250, 824).—A discussion of the general significance of auto-oxidation and anti-oxygen action in biology. The mechanism of the auto-oxidation of acetaldehyde and its inhibition by anti-oxygens is also discussed. It is supposed that acetaldehyde exists in two forms, one of which is very reactive and auto-oxidisable. The effect of an anti-oxygen is to catalyse the transformation of the reactive into the non-reactive form.

G. W. R.

**Isolation of the Thyroid Hormone.** BENNO ROMEIS (*Biochem. Z.*, 1922, 133, 97—111).—Thyroid gland is hydrolysed by boiling with a solution of barium hydroxide for five to six days, so that the biuret test disappears. The precipitate formed on acidifying with hydrochloric or acetic acid is purified by dissolving in dilute alkali, and reprecipitating several times by acidifying. The precipitate is extracted with 90% alcohol containing acetic acid, and on evaporating the alcohol, a precipitate separates, which is again submitted to the process of extraction by alcohol

containing acetic acid and by precipitation. This is repeated several times, and the resulting material is washed with ethyl ether and with light petroleum, and then consists of a very light brown powder, with a high iodine content. This substance resembles Kendall's thyroxin, to which it appears to be closely related. It is possibly even more active physiologically. W. O. K.

**Energy Exchanges in Muscle.** OTTO MEYERHOF (*Plüger's Archiv*, 1922, 195, 22—74; from *Chem. Zentr.*, 1922, iii, 1235—1236; cf. A., 1922, i, 897).—An investigation into the origin of the approximately 400 cal. liberated in the formation of 1 g. of lactic acid from glycogen (caloric quotient of lactic acid). The heat of combustion of lactic acid, estimated by way of zinc lactate, is 325,700 cal. per mol. The average caloric quotient of lactic acid with electrical stimulation is 370 cal. With cut muscle in a phosphate solution, the value is only 200 cal.; this is in fair agreement with the value calculated from the heat of decomposition of glycogen, the heat of dilution of lactic acid, and the heat of reaction with the phosphate. The extent to which lactic acid goes into solution influences the amount of heat developed. The heat of reaction of lactic acid with substances in intact muscle is affected by hydrogen-ion concentration. The difference between the heat of reaction of lactic acid in muscle (190—200 cal.) and with buffered solutions of amino-acids (130 cal.) or protein solutions (137—140 cal.) is attributed to changes in the state of ionisation of proteins in a non-aqueous phase. The temperature coefficient of lactic acid (per 10°) in cut muscle is 2—3, in intact muscle about 4. G. W. R.

**The Influence of Cooling on the Creatine in Muscle.** ALEXANDER PALLADIN and ANNA KUDERJAVZEV (*Biochem. Z.*, 1922, 133, 89—96).—There is a marked increase of creatine in the muscles of a rabbit if it is killed several hours after its body temperature has been reduced from 39° to about 30° by immersion for some time in a cold bath. This increase, of the order of 0.1%, reaches a maximum about twelve hours after the cooling, and there follows a slow return to normal. W. O. K.

**The Decomposition of Carbohydrates in Transversely Striped Muscles. III.** FRITZ LAQUER and PAUL MEYER (*Z. physiol. Chem.*, 1923, 124, 211—226; cf. A., 1922, i, 1089).—The effect of fresh frog's muscle in converting various carbohydrates into lactic acid has been investigated. The greatest activity is shown when acting on glycogen, followed by levulose, starch, dextrose, and mannose. All the other carbohydrates tested, galactose, sorbose, sucrose, maltose, diamylose, and tetramylose (obtained from starch by the action of *Bacillus macerans*), inulin and Merck's "Karamose" give insignificant yields of lactic acid. Thus if there is a reactive form of carbohydrate present in glycogen as previously suggested (*loc. cit.*), it does not appear to be any of the above. W. O. K.

**The Effect of Histozyum on the Homologues of Hippuric Acid.** I. A. SMORODINCEV (*Z. physiol. Chem.*, 1923, 124, 123—139).—Histozyum, which effects the hydrolysis of hippuric acid, appears in the kidneys and skeletal muscles of dogs and also markedly in the kidneys of pigs. It is also present in the spleen, lungs, heart, and skeletal muscles of dogs, but not in the liver, and is found in the liver of calves, oxen, and horses. It is almost insoluble in water and in aqueous glycerol. Besides hippuric acid, histozyum hydrolyses also *d*- $\alpha$ -benzamidobutyric acid and *l*-benzoyl-leucine, but not  $\beta$ -benzoylalanine, *dl*- $\beta$ -benzamidobutyric acid, benzamidoisobutyric acid, and *l*- $\beta$ -benzamidobutyric acid. Glycocholic acid and taurocholic acid are hydrolysed with the separation of cholic acid.

W. O. K.

**Faulty Diet and its Relation to the Structure of Bone.** P. G. SHIPLEY (*J. Amer. Med. Assoc.*, 1922, 79, 1563).—Among the dietetic principles concerned in the growth of bone are: (1) an uncharacterised organic substance, distinct from fat-soluble vitamin-*A*, and found in certain fish liver oils and in small amounts in butter and coconut oil, (2) calcium, (3) phosphorus, (4) water-soluble vitamin-*B*, (5) fat-soluble vitamin-*A*. Water-soluble vitamin-*C* influences the structure of the bone of the guinea pig, but not of the rat. Inadequacy of fat-soluble vitamin-*A* causes perfect calcification, but a high degree of osteoporosis develops; deficiency of water-soluble vitamin-*B* causes similar results. If the organic substance so abundantly present in fish oils is freely supplied, rickets will not develop in spite of a faulty ratio of calcium to phosphorus in the food. It is found that the shorter ultra-violet rays have an important antirachitic effect.

CHEMICAL ABSTRACTS.

**Decalcification of Teeth and Bones, and Regeneration of Bone through Diet.** P. R. HOWE (*J. Amer. Med. Assoc.*, 1922, 79, 1565—1567).—The magnesium content of sound teeth, when estimated by Tisdall and Kramer's method (*A.*, 1921, ii, 655), was found to range from 0.554 to 0.764% (average 0.649%), whilst decayed teeth contained 0.825 to 1.585% (average 1.154%). With all the proper food factors supplied except the antiscorbutic, the animal organism appears to withdraw calcium from the teeth and from some parts of the bone.

CHEMICAL ABSTRACTS.

**Tin in the Human Organism.** ÉMILE MISK (*Compt. rend.*, 1923, 176, 138—141).—Tin may be estimated in human organs by two methods. In the first, 100 g. of the pulped material and 1 g. of calcined magnesia are evaporated with 30 c.c. of 30% magnesium nitrate and the residue after drying at 250° is ignited at a dull red heat to a white ash, which is then fused with 2—3 g. of potassium hydroxide. The cold mass is extracted with water, and after filtration the filtrate is evaporated and the residue treated with nitric acid and the tin weighed as stannic oxide. In the second method, 100 g. of the material are evaporated with

50 c.c. of 30% potassium hydroxide and the residue heated to fusion, the cold mass then being treated as described above.

Tin exists normally in the human organism, and the liver has highest content, being followed by the stomach, kidneys, lungs, and brain. 0.03—0.04 g. of tin in 100 g. of human viscera is not excessive in amount. W. G.

**Glycogen Content of certain Invertebrates and Fishes.** L. G. KILBORN and J. J. R. MACLEOD (*Quart. J. Exp. Physiol.*, 1920, 12, 317—330).—By Pflüger's method, the following percentages of glycogen were found in the (moist) digestive glands (hepatopancreas): Asteroidea, 0.232 to 1.52; Lamellibranchiata, 0.31 to 1.56; Crustacea, 0.05 to 1.39; Elasmobranchii, 0.0 to 0.21; Teleostomi, 0.0 to 6.5. Feeding conditions and season seem partly responsible for the varying amounts. In the (moist) muscles the following percentages of glycogen were found: Lamellibranchiata, 0.077 to 2.67 (the latter in the adductor muscles); Crustacea, trace to 0.36; Elasmobranchii, 0.0 to 0.018; Teleostomi, 0.0 to 0.29. In all cases when it was possible to obtain a sufficient amount of heart muscle, the glycogen content was found to be several times greater than that of other muscles, and sometimes greater than that of the liver; thus in the lobster 0.85—1.42% was found in the heart muscle, while the other muscle content was 0.36%. In several cases, the glycogen was found to yield a sugar fermentable by yeast after hydrolysis. In other cases, part of the reducing material seemed to consist of other substances.

#### CHEMICAL ABSTRACTS.

**Concentration of Urea in Saliva.** P. S. HENCH and MARTHA ALDRICH (*J. Amer. Med. Assoc.*, 1922, 79, 1409—1412).—The combined urea- and ammonia-nitrogen values of the saliva are normally between 6 and 13 mg. per 100 c.c. These combined values closely approximate to those of the urea-nitrogen in the blood. In urea retention, the combined urea- and ammonia-nitrogen always increase with an increase in the blood urea-nitrogen.

#### CHEMICAL ABSTRACTS.

**Effect of Magnesium Sulphate on the Secretion of Bile.** EMMETT B. FRAZER (*J. Amer. Med. Assoc.*, 1922, 79, 1594—1596).—When introduced directly into the duodenum, or into the circulation, magnesium sulphate does not cause any change in the character of the bile, although in some instances the rate of flow was retarded.

#### CHEMICAL ABSTRACTS.

**The Solubility of Gallstones.** ANNE ROSIN (*Z. physiol. Chem.*, 1923, 124, 282—286).—Cholesterol gallstones are soluble to some extent in solutions of salts of bile acids, more particularly in solutions of sodium deoxycholate. W. O. K.

**The Excretion of Uric Acid on a Diet Poor in Purines.** H. STEUDEL (*Z. physiol. Chem.*, 1923, 124, 267—273).—The endogenous uric acid in the urine depends on the condition of the contents of the intestine. The urine of an individual whose faeces

showed fermenting powers was abnormally poor in uric acid, this being due apparently to destruction of the purine substances in the intestine.

W. O. K.

**The Rôle of the Effect of Acids in the Production of Adrenalin Hyperglycæmia.** F. KORNFELD and H. ELIAS (*Biochem. Z.*, 1922, 133, 192—211).—After the injection of adrenalin into rabbits, dogs, or human beings, there is only a very slight lowering of the carbon dioxide tension of the blood or in the case of men of the alveolar carbon dioxide tension (sometimes even this slight lowering is absent), but nevertheless there is marked hyperglycæmia. There is therefore no reason to believe that the hyperglycæmia is in any way due to the hypokapnia. W. O. K.

**The Formation of Conjugated Glycuronic Acids after Administration of Elbon.** KIVOSHI MORINAKA (*Z. physiol. Chem.*, 1923, 124, 247—252).—The urine of rabbits to which have been given by the mouth 2 g. of elbon (cinnamoyl-*p*-hydroxyphenylcarbamide) per day for a long time contains hippuric acid and also a levorotatory substance, isolated as the potassium salt, orange, colourless prisms, shown to be the potassium salt of *p*-hydroxyphenylcarbamideglycuronate, m. p. 231°, decomp.,  $[\alpha]_D^{20} -74.99^\circ$  in water. On hydrolysis with acid, glycuronic acid and *p*-aminophenol are obtained, the latter derived by the further hydrolysis of the *p*-hydroxyphenylcarbamide formed initially. W. O. K.

**[Physiological Action of Dialkyl- and Alkylaryl-barbituric acids.]** H. A. SHONLE and A. MOMENT (*J. Amer. Chem. Soc.*, 1923, 45, 243—249).—See this vol., i, 248.

**Comparative Toxicity of Different Acids towards Fish Sticklebacks.** (MILÉ) FRANCE GUEYLARD and MARCEL DUVAL (*Compt. rend.*, 1922, 175, 1243—1245).—In order to study the influence of acids on aquatic animals and to ascertain whether any toxic effect could be attributed solely to hydrogen-ion concentration, sticklebacks (*Gasterosteus aculeatus* var. *leirurus*) were placed in a series of solutions of acetic, lactic, propionic, and phosphoric acids of different hydrogen-ion concentration and the time of survival was noted. A diagram is given showing the curve obtained for each acid on plotting its  $p_H$  value against survival time in hours. The latter varies considerably with the  $p_H$  value, increasing slowly at first and then very rapidly with diminution in the concentration of hydrogen-ions, but the nature of the acids exerts considerable influence. For example, when  $p_H = 4$ , the fish live for more than eight hours in phosphoric acid, for one and a half hours in lactic acid, eleven minutes in acetic acid, and less than nine minutes in propionic acid.

H. J. E.

## Chemistry of Vegetable Physiology and Agriculture

**Activation of Hydrogen and Carbon Dioxide Assimilation by Bacteria.** W. RUHLAND (*Ber. Deut. bot. Ges.*, 1922, 40, 180—184).—The power of utilising the chemical energy of free hydrogen for carbon dioxide assimilation is widely distributed amongst bacteria. Contrary to opinions previously advanced that the carbon dioxide is first reduced by the activated hydrogen, a slow direct combustion of hydrogen occurs which furnishes the energy for the carbon dioxide reduction. This occurs, as with green plants, with the elimination of oxygen. Hidden by the hydrogen combustion, a slow exhalation of carbon dioxide occurs, involving the consumption of both free and combined oxygen. The presence of iron is essential for the assimilation, and it must be in combination as hydrogen carbonate. If carbon dioxide is excluded from the gaseous atmosphere of inorganic cultures, very little or no hydrogen is assimilated. The ratio of the volumes of hydrogen to oxygen consumed is in the youngest cultures less, but, later, greater than 2, the variation depending on the intensity of carbon dioxide exhalation. The maximum hydrogen assimilation occurs in weak alkaline solutions, and falls off rapidly on both sides to the respective limits of  $p_H=5.3$  and  $p_H=9.1$ . The protective action of many organic substances, for example, dextrose, against hydrogen assimilation is due to the rapid formation of acids to which they give rise, which causes the disappearance of the  $HCO_3^-$  ion, which alone can be assimilated. The utility of the hydrogen combustion expressed by the "economic quotient," Organic substance produced/Hydrogen and oxygen used, varies considerably, and is greatest in approximately neutral solution. With the same hydrogen-ion concentration and otherwise similar conditions, it is approximately proportional to the hydrogen and oxygen used up.  
G. F. M.

**The Microbic Metabolism of Lactic Acid and Pyruvic Acid.** E. AUBEL (*Compt. rend.*, 1923, 176, 332—335).—The author has isolated an organism from the Paris water supply which, when grown on a solution of dextrose and suitable mineral salts, produces during the first few days pyruvic acid and no lactic acid, but in the following days the pyruvic acid disappears and lactic acid makes its appearance. When the culture is on a similar medium, but the sugar is replaced by sodium pyruvate, the pyruvic acid slowly disappears and there is found in the medium acetic acid, an acid soluble in ether and giving the Hopkins reaction but only present in small amount, and a crystalline acid, m. p.  $152^\circ$ , not identified. When in the same medium the sodium pyruvate is replaced by calcium lactate, a portion of the lactic acid is converted into acetic acid and acetaldehyde, but pyruvic acid could not be detected.  
W. G.

**Growth and Respiration of Sulphur-oxidising Bacteria.**

SELMAN A. WAKSMAN and ROBERT L. STARKEY (*J. Gen. Physiol.*, 1923, 5, 285—310).—*Sulphomonas thio-oxidans* oxidises sulphur to sulphuric acid or sodium thiosulphate to sulphate, and at the same time absorbs atmospheric carbon dioxide as a source of carbon. The ratio between the sulphur oxidised and the carbon dioxide reduced is 31·8:1 and 64·2:1 in the cases of sulphur and thiosulphate, respectively. Excess of sulphur in the medium does not inhibit the oxidation, but nitrates have a strong inhibiting action. Dextrose is likewise innocuous, but peptone almost completely stops sulphur oxidation in 1% concentration. The injurious effect of acid becomes marked only at concentrations exceeding 0·5*N*. The optimum  $p_H$  for growth is between 2·0 and 5·5. The zone is sharply limited on the alkaline, but not on the acid side.

W. O. K.

**The Action of Saponin Substances on the Plant Cell.**

FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1922, 40, 249—253).—Cyclamin and digitonin in feeble concentration slightly increase the fermentative activity of the yeast-cell, in higher concentration they strongly retard it. This physiological action of these saponins is due to the formation of chemical compounds with the lipoids in the protoplasm, which are thereby inactivated, and the structure of the protoplasm is disturbed by the flocculation of the saponin-cholesteride. A slight modification of the lipid structure, insufficient to cause flocculation, increases the zymase activity, on the other hand, partly by increasing the permeability, and partly perhaps by removing retarding substances. Certain combinations of saponins such as quillaia saponin and digitonin are distinctly less poisonous than digitonin alone, and the combination digitonin-sodium glycine actually leads to increased zymase activity, which is to be attributed to the strong solvent action of the latter substance on lipoids, preventing the precipitation of the cholesterol and the consequent destruction of the cell-structure. No parallel could be traced between the surface activity and the chemical activity of the various saponins.

G. F. M.

**The Synthesis and Degradation of Asparagine in Plants.**

D. PRIANISCHNIKOV (*Ber. Deut. bot. Ges.*, 1922, 40, 242—248).—Whilst, as has already been shown, etiolated seedlings of Graminaceae and other plants can readily synthesise asparagine from ammonia presented in the form of a dilute solution of ammonium chloride or sulphate, and certain Leguminosae can effect the same synthesis only when calcium carbonate is also present, the yellow lupine showed under similar conditions a quite abnormal behaviour, no asparagine was formed, the normal asparagine content of the plant decreased, and the ammonia content became abnormally great, giving the cell juice an alkaline reaction. The presence of calcium carbonate only accentuated this phenomenon. This abnormal behaviour is entirely attributable to lack of carbohydrates, as on the one hand other plants were also shown to behave in this

abnormal way under an artificially created deficiency of carbohydrates, and on the other yellow lupine seedlings to which carbohydrates were supplied, either by utilising the green plants instead of etiolated plants for the experiments, or by feeding etiolated plants with dextrose solutions, behaved normally; that is to say, the asparagine-nitrogen increased, and the ammonia-nitrogen decreased. It follows, therefore, that it is not a peculiarity of the species but the conditions of nutrition which is the determining factor for the asparagine synthesis. Only when a carbohydrate or fatty carbon chain is present can the plant convert ammonia into asparagine and thence into amino-acids and proteins, otherwise ammonia accumulates, and the plants show the symptoms of ammonia poisoning. Asparagine is to be regarded as the analogue in the vegetable kingdom of carbamide in the animal kingdom. It is pointed out that the process is reversible, and in absence of carbohydrates degradation of protein to asparagine or glutamine, and finally to ammonia, occurs.

G. F. M.

**Incrustive Substances of Plants. III.** ERICH SCHMIDT, EBERHARD GEISLER, PAUL ARNDT, and FRITZ IHLOW (*Ber.*, 1923, 56, [B], 23—31; cf. A., 1921, i, 912; 1922, i, 206).—Further examination has confirmed the previous observation that aqueous solutions of chlorine dioxide are specific reagents for the removal of botanical incrustations. The cell-membranes of the higher fungi, archegoniates, and phanerogams are thus shown to be composed of tissue containing chitin or cellulose accompanied by hemicelluloses and pentosans and incrustation containing hexosans and pentosans accompanied by those portions of the cell-membrane which are attacked by chlorine dioxide.

The concentration of the chlorine dioxide solution (about 6%) is considerably greater than that recommended previously (*loc. cit.*). Its preparation from potassium chlorate, crystalline oxalic acid, and sulphuric acid is described in detail. Like the more dilute solution, it is without action on the tissue of plants.

For the removal of incrustations, the finely divided portions of plants are treated with an approximately 6% aqueous solution of chlorine dioxide in closed bottles at the atmospheric temperature in diffused daylight during seventy-two hours with occasional agitation. The precipitate is filtered and the residue mechanically agitated with water and again filtered. The combined filtrates are well stirred in a large porcelain dish to remove chlorine dioxide, and are afterwards dialysed against running water for at least forty-eight hours; they are subsequently evaporated to dryness under diminished pressure. The original residue is treated with a hot aqueous solution of crystalline sodium sulphite (2%) and the mixture filtered. The residue is thoroughly washed and the united filtrate and wash waters are dialysed against running water for at least seventy-two hours. They are subsequently evaporated to dryness under diminished pressure and the residue is united with that obtained by the treatment with chlorine dioxide. The product is separated by means of boiling absolute alcohol into

insoluble polysaccharides which usually contain 5–10% of ash (this cannot readily be removed by dialysis, but is reduced to about 1.5%, consisting chiefly of silica, by electro-osmosis) and soluble components of the membrane which are attacked by chlorine dioxide.

The method described previously (*loc. cit.*) for the preparation of skeleton substance completely free from incrustation requires to be supplemented by a second treatment with chlorine dioxide solution (0.2%) and sodium sulphite (2%). The residue is well filtered and placed first in alcohol and then in ether for about twenty-four hours. After being dried in a desiccator, it is thus obtained as a spongy material.

The quantitative estimation of tissue and incrustation is modified and carried out in small pressure bottles according to the process outlined above. Beech wood is thus shown to contain 54.09% of tissue and 45.91% of incrustation.

H. W.

**Amylase in Plants. I. The Production and Behaviour of Amylase in Living Plants.** KNUT SJÖBERG (*Biochem. Z.*, 1922, 133, 218–293).—Following Euler and Svanberg (*A.*, 1919, i, 614), the author finds that the amylolytic activity of plant preparations is conveniently measured as  $S = km/P$ , where  $k$  is the mean value of the reaction coefficient, calculated as a unimolecular reaction,  $m$  is the maximum weight of maltose produced, and  $P$  is the weight of the preparation applied, the maltose being produced from the starch by the preparation under standard conditions as regards  $p_H$  and temperature. From measurements of the maltose at various times,  $k$  is calculated. The optimum  $p_H$  for plant diastase is from 5 to 5.4. During the ripening of seeds there occurs a very marked increase of the amylase. Various plants at various seasons have been investigated, and it is found that the amylase activity varies very greatly, being greatest in young leaves. Algæ increase in amylase when nourished in a solution containing starch, calcium lactate, or calcium tartrate, whereas a decrease occurs if the solution contains sucrose, lactose, maltose, glucose, or galactose. Generally speaking, there is no correlation between the content of a plant in amylase, and in starch, or in sugar.

W. O. K.

**Amylase in Plants. II. The Sensitiveness of the Amylase of *Phaseolus vulgaris* to Temperature.** KNUT SJÖBERG (*Biochem. Z.*, 1922, 133, 294–330).—An investigation of the amylase of *Phaseolus vulgaris* shows that there are two enzymes concerned in the conversion of starch into sugar. The rate of disappearance of starch has the same temperature constant,  $A = \log(k_2/k_1)T_1T_2/0.4343(T_2 - T_1)$  between 20° and 40° of about 9600, follows the law of a unimolecular reaction, and, moreover, the enzyme causing the disappearance of the starch is destroyed by sodium chloride. On the other hand, the rate of formation of sugar has a temperature constant varying from 10,000 at 20°, to 5700 at 40°, its inactivation does not follow the law of a uni-

molecular reaction, and there is no inhibition by sodium chloride. For the formation of sugar, the optimum  $p_H$  is from 5 to 5.5, and for the disappearance of starch it is from 4 to 6. The amylase is most stable at  $p_H$  6.5–7.0. The temperature at which the enzymes are wholly destroyed is  $45^\circ$  for both enzymes. W. O. K.

[Constituents of] Cork. P. KARRER, J. PEYER, and ZORRA ZEGA (*Helv. Chim. Acta*, 1922, 5, 853–863).—The carbohydrates contained in cork were studied in the course of an attempt to characterise in a more satisfactory manner than heretofore the constituents of cork. After removing the alcohols by extraction with solvents and hydrolysing with alcoholic potash to remove fatty acids, a residue was left equal to about 8% of the weight of the original air-dried cork. When this was treated with acetic anhydride and anhydrous zinc chloride at  $50$ – $60^\circ$ , part of it went into solution, and when the solution was poured into water a precipitate resembling cellulose acetate was thrown down. It had  $[\alpha]_D^{20}$   $-21.2^\circ$  to  $-22.1^\circ$  and on hydrolysis gave dextrose. By repeating the process several times on the cork residue, less pure fractions with a smaller laevorotation were obtained. The total yield obtained was about 12.1 g. of acetyl product from 430 g. of original cork. From it a very small quantity of crystalline cellobiose octa-acetate was obtained. A similar yield of acetyl compound was obtained by treating unhydrolysed cork with acetic anhydride and zinc chloride. Since the residue retained all the properties of the original cork, it is concluded that the carbohydrates cannot play any important part in the structure of the cork. It has been suggested by Grün and Wittka (*A.*, 1922, i, 114) that cellulose esters of higher fatty acids may be constituents of cork-like substances. The properties of such substances as cellulose hexapalmitate, however, do not resemble those of cork. The following are described.

*l*-Glucosan tripalmitate,  $C_{54}H_{100}O_8$ , prepared by the action of palmityl chloride on *l*-glucosan in chloroform solution in presence of quinoline, forms fine, white needles, m. p.  $68.5^\circ$ ,  $[\alpha]_D^{20} -21.08^\circ$ . *l*-Glucosan tristearate,  $C_{60}H_{112}O_8$ , prepared in the same way as the last, m. p.  $73.4^\circ$ ,  $[\alpha]_D^{20} -18.4^\circ$ . Cellulose hexapalmitate,

$C_{12}H_{14}O_{10}(CO-C_{15}H_{31})_6$ , prepared in a similar way, is a white, amorphous substance, m. p.  $78^\circ$ ,  $[\alpha]_D^{20} -3.0^\circ$ . E. H. R.

The Starch of Floridean Algæ. G. MANGENOT (*Compt. rend.*, 1923, 176, 183–185).—In the main a discussion of the subject from the point of view of plant physiology. The starch of the Florideæ, both from the chemical and physiological point of view, behaves like typical starch, except that its colour with iodine in potassium iodide distinguishes it slightly. W. G.

Biochemical Study of the *Laminaria*. Variations in the Chief Constituents. Their Relationships, Dependence on External Conditions, and their Functions. P. FREUNDLER, (Mlle) LAURENT, and (Mlle) MÉNAGER (*Bull. Soc. chim.*, 1922, [iv], 31, 1341–1347; cf. *A.*, 1922, i, 98).—Further examination

of certain species of *Laminaria* shows that at the end of winter they are all completely deprived of carbohydrate reserve material, which in September attained a maximum of about 40%. At this period also the perennial *Laminaria* contain little or no "fixed" iodine. The energy for the early spring growth is thought to be provided by a reserve of iodine which is stored up by means of a special pigment which is not found in the annual algæ, and is transported to the growing areas by means of the algin. A lack of sunshine, as in 1922, is accompanied by a considerable diminution of iodine in certain regions, but it is not so pronounced in places under the influence of warm ocean currents. The greater part of the iodine in the algæ is present in unstable organic combination, but it was found that the amount that could be estimated by incineration increased spontaneously on keeping. Closely associated with the iodine are a yellow pigment decolorisable by sodium hydrogen sulphite, and a red pigment found only in deep-water algæ, which is insoluble in the sulphite, but soluble in ammonia with an intense red colour. The algin appears to act as salt concentrators. They absorb, for example, 20–25% of their weight of calcium or alkali metal chlorides, giving insoluble gels (alkali alginates). The presence of hydrolysing and alcohol-forming enzymes was established.

G. F. M.

**Phycocerythrin in the Myxophyceæ.** N. WILLE (*Ber. Deut. bot. Ges.*, 1922, 40, 188–192).—The occurrence is recorded of a phycocerythrin in a species of Myxophyceæ, identified as *Phormidium persicinum* growing 3–4 fathoms deep off the south coasts of Norway, which gives an absorption spectrum identical with that of the phycocerythrin found in the Floridææ, and is undoubtedly identical in other respects with that substance. A phycocerythrin has already been detected by Boresch in other species of Myxophyceæ, but this was apparently different from the colouring matter of the Floridææ, as it showed only one absorption band in the green, whilst the colouring matter of *P. persicinum* shows three bands, that near the F line being particularly characteristic of the phycocerythrin of the Floridææ.

G. F. M.

**The Pigment of the Alga *Palmellococcus miniatius*, Chod., var. *porphyrea*, Wille.** K. BORESCH (*Ber. Deut. bot. Ges.*, 1922, 40, 288–291).—The water-soluble pigment which occurs in a species of *Palmellococcus* found growing in moist places in the Botanical Garden in Prague and identified by Wille as *P. miniatius*, Chod., var. *porphyrea*, was identified by its absorption spectrum and reactions as a mixture of phycocyanin, and the phycocerythrin characteristic of the Schizophyceæ. The identity of the pigments in such widely-separated groups of algæ points to the common chemico-physiological relationship of plants.

G. F. M.

**The Occurrence of *d*-Quercitin in the Seed Kernels of *Achras sapota*, L.** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1922, 41, 784–786).—*d*-Quercitin together with the saponins was

extracted from the dried and powdered seeds by means of methyl alcohol and separated from the saponins by precipitation with ether followed by extraction of the precipitate with methyl alcohol. The product was shown by various tests to be identical with the *d*-quercitin obtained from acorns. The author states that the mixture of lactose and sucrose obtained by Bouchardat (A., 1871, 1915) from the sap and also from the ripe fruit of *Achras sapota* was in reality a mixture of sucrose with quercitin. H. J. E.

**The Localisation of the Hydrocyanic Acid Glucosides and of Emulsin in Bitter Almonds and in Cherry-laurel Leaves.** L. ROSENTHALER and K. SEILER (*Ber. Deut. pharm. Ges.*, 1922, 32, 245—248).—A method is described for the microscopic detection of hydrocyanic acid from the glucoside and emulsin in the plant-tissues (cf. *Schweiz. Apoth. Ztg.*, 1922, 60, 477). In bitter almonds, both amygdalin and emulsin are found in all tissues except the shell. Detailed data are given of the distribution of prulaurasin and emulsin in the leaves of the cherry-laurel at the beginning of March. In general, both substances occur in the same tissues, although there are some in which prulaurasin is found without emulsin. Where the emulsin and the hydrocyanic acid glucoside are present in the same cell and yet do not react, there must be some internal separation of them within the cell.

P. M.

**The Odorous Constituents of Apples. II. Evidence of the Presence of Geraniol.** FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1922, 44, 2938—2942).—An examination of the essential oil from the parings of McIntosh apples, a particularly fragrant variety of the fruit, confirms the results of a previous investigation (A., 1920, i, 653), that the odorous constituents of apples consist chiefly of amyl esters, but in addition proof of the presence of geraniol was obtained. It is probable that geraniol either in the free state or in the form of esters is contained in varying amounts in all apples, but is more abundant in those varieties which possess its distinctive odour.

W. G.

**The Constituents of the Benzene Extract of American Cotton.** ROBERT GEORGE FARGHER and MAURICE ERNEST PROBERT (*J. Text. Inst.*, 1923, 14, T., 49—65).—The material at the disposal of the authors was obtained by heating approximately two tons of American cotton with commercial "90% benzol" in a rotating kier by means of steam at 40 lb. pressure, and consisted, therefore, of the material extracted with benzene, together with that removed by the condensed steam. The crude product was dried at 100° in a vacuum, when it was left as a dark brown solid wax. On the laboratory scale, the benzene extract amounted to 0.51% of the dried cotton.

The crude wax was mixed with purified sawdust and extracted by light petroleum, ether, benzene, alcohol, and chloroform, and

the extracts were submitted to exhaustive examination, which is described in detail. The following substances were isolated.

*Alcohols*.—Gossypyl alcohol is the chief constituent; montanyl alcohol occurs in smaller amount, and carnaübyl alcohol, ceryl alcohol, sitosterol, and  $\alpha$ - and  $\beta$ -amyryns are also present. Sitossterolin, the glucoside, was also encountered. *Acids*.—Palmitic, stearic, and oleic acids occur in the free state; montanic, cerotic, palmitic, and stearic acids, and a new acid, occur as salts, chiefly of sodium; whilst carnaübic, palmitic, stearic, and oleic acids, and a lower homologue of oleic acid are present as esters. *Hydrocarbons*.—Triacontane and hentriacontane have been isolated, but the bulk of the hydrocarbons present are liquid.

*Gossypyl alcohol*,  $C_{30}H_{62}O$ , is the chief constituent of the benzene extract. It occurs in three forms, differing in solubility, but yielding the same derivatives. The  $\alpha$ -form, which is the least soluble, crystallises in feathery needles, m. p. 87—88°; the  $\beta$ -form separates in leaflets, m. p. 85—87°; and the  $\gamma$ -modification forms small leaflets, m. p. 82—83°. On recovery from the acetate, the  $\alpha$ -form appears to have changed into the  $\beta$ -modification. *Gossypyl acetate* forms small, silky needles, m. p. 68—69°; the *benzoate* is a felted mass of minute needles, m. p. 65°; the *p-bromobenzoate* forms clusters of needles, m. p. 66—67°; and the *p-nitrobenzoate* crystallises in tufts of needles, m. p. 72°. The various forms of the alcohol all gave the same acid on fusion with potash-lime. *Gossypic acid*,  $C_{30}H_{60}O_2$ , crystallises in radiating clusters of needles, m. p. 85—86°; the *methyl ester* has m. p. 68—69°, the *ethyl ester*, m. p. 66—66·5°, the *amide*, m. p. 108—109°, and the *anilide*, m. p. 99·5°.

*Montanyl alcohol*,  $C_{28}H_{58}O$ , crystallises as a mass of minute needles, m. p. 85—86°; its *acetate* forms clusters of leaflets or needles, m. p. 69°; the *benzoate* has m. p. 66—67°; the *p-bromobenzoate* is a mass of minute needles, m. p. 66—66·5°; and the *p-nitrobenzoate* has m. p. 70—70·5°. On fusion with potash-lime, the alcohol yielded montanic acid which was completely identified with a sample from montan wax.

Both gossypyl and montanyl alcohols obstinately retain water, even when heated for some hours at 115° in a vacuum. The anhydrous forms were obtained by saponification of the acetates. This tendency necessitated a careful examination of their derivatives, and conversion into the substituted benzoates and the corresponding acids proved to be the best means of characterising the alcohols. Furthermore, molecular-weight determinations were successfully made by saponifying the esters and titrating.

Of the acids present, carnaübic acid and the new acid are worthy of mention. The former has been definitely characterised. It crystallises in leaflets, m. p. 72—73°; the *methyl ester* has m. p. 55—56°, the *ethyl ester*, m. p. 52—53°; the *amide*,  $C_{23}H_{47}\cdot CO\cdot NH_2$ , m. p. 103·5°; and the *anilide*, m. p. 94—94·5°. The new acid,  $C_{34}H_{68}O_2$ , is possibly identical with an acid found by Schalfée in 1876, associated with the melissic acid of beeswax; it separates in fern-like clusters, m. p. 90—91°; the *methyl ester* has m. p. 75—76°, the *amide*, m. p. 108—109°, and the *anilide*, m. p. 105°.

The liquid hydrocarbons were divided into five fractions boiling between 170° and 220°, under 28 mm., and five more with b. p. 150—210°/1 mm. All the oils were pale yellow and reacted with a solution of bromine in chloroform. Densities and refractive indices are recorded. J. C. W.

***Stenocalix pitanga*, Berg, or *Eugenia pitanga*, Berg-Arech (Pitanga or Nangapire).** VÍCTOR COPPERTI and MATÍAS GONZÁLEZ (*Anal. Fis. Quím.*, 1922, 20, 406—419).—The leaves of *Eugenia pitanga*, a Uruguayan tree, yield an essential oil, which contains as its principal constituents citronellol, geranyl acetate, geraniol, cineol, terpinene, sesquiterpenes, and polyterpenes. A resin also occurs composed of resin acids, resens, and resinotannols. Alkaloids, glucosides, bitter principles, and other neutral substances are absent. The leaves are not toxic. G. W. R.

**Examination of Authentic Grape Juices for Methyl Anthranilate.** FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Agric. Res.*, 1923, 23, 47—53).—Grapes usually regarded as representing pure-bred *Vitis labrusca*, which includes the concord, the commonest variety grown in the Eastern States of America and used for edible purposes and the preparation of unfermented grape juice, all contain methyl anthranilate. With few exceptions it was also found in varying amounts in hybrids of *V. labrusca*, especially when this species predominates. On the other hand, this ester could not be detected in juices from Californian grapes which are derived from *V. vinifera*, the European cultivated species, nor from *V. rotundifolia*, the species grown in the Southern States. It is suggested that the presence or absence of methyl anthranilate may possess some diagnostic value in determining the botanical relationship of varieties of uncertain origin. In those varieties in which it occurs methyl anthranilate doubtless imparts a distinctive odour, but it does not completely account for the entire aroma, and a complete chemical examination of the odorous constituents still remains to be accomplished. G. F. M.

**The Presence of Aucubin and Melampyritol [Dulcitol] in some Species of Melampyrum.** (Mlle) MARIE BRAECKE (*Compt. rend.*, 1922, 175, 990—992; cf. Bridel and Braecke, A., 1922, 1, 209, 799).—Following the extraction of aucubin from *Melampyrum arvense*, an attempt was made to ascertain whether it is present in other species, and also whether dulcitol, present in *M. nemorosum* and *M. arvense*, could be found. Aucubin was obtained in pure condition from *M. cristatum*, *M. nemorosum*, and *M. pratense*; dulcitol is present in *M. cristatum*, but was not obtained from *M. pratense*. H. J. E.

**Confirmation of the Occurrence of Linalyl Esters in Peaches.** FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1922, 44, 2966—2967; cf. A., 1922, 1, 99).—In addition to the formation of citral by the oxidation of the alcohol

mixture arising from the saponification of the esters obtained from peaches the authors have now proved the presence of acetone and lævulinic acid in the products of oxidation. These substances were also obtained by the oxidation of linalool itself, and thus confirmation of the presence of linalyl esters in peaches was obtained.

W. G.

**The Enzymes of the Latex of the Indian Poppy (*Papaver somniferum*).** HAROLD EDWARD ANNETT (*Biochem. J.*, 1922, 16, 763—769).—The latex of the Indian opium poppy has a powerful oxidising action on guaiacum tincture, pyrogallol, benzidine, and tyrosine in the absence of hydrogen peroxide. The reaction is inhibited by the presence of this reagent. The actions on benzidine and tyrosine are particularly powerful. The dialysed latex before and after filtration also oxidises the above reagents. Opium powder stored for three years contains an oxidising enzyme which acts on benzidine. It is suggested that the loss of morphine in dry opium powder on storage may be due to the action of oxidising enzymes. Amylase, invertase, maltase, emulsin, and urease are absent from the latex, which shows, however, a weak proteolytic activity.

S. S. Z.

**The Bark of *Tiliacora acuminata*, Miers.** L. VAN ITALLIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1922, 59, 1381—1388).—Among the products obtained from the alcoholic extract of the dry powdered bark is a new alkaloid, *Tiliacorine*, of m. p. 260—261°, decomp.,  $\alpha_D +105.3^\circ$ , and composition  $C_{30}H_{27}O_3N(OMe)_2$ . The methoxy-groups were estimated by Zeisel's method, but no other light could be obtained on the constitution. (See *J.S.C.I.*, 1923, 159A.)

S. I. L.

**The Presence of Aucubin in the Seeds of *Veronica hederæ-folia*, L.** C. CHARAUX (*Bull. Soc. Chim. biol.*, 1922, 4, 568—570).—A glucoside, isolated from the seeds of *Veronica hederæ-folia* by extraction with alcohol in presence of calcium carbonate, has been identified as aucubin, m. p. 180°,  $[\alpha]_D -163.5^\circ$ . W. O. K.

**The Chemical Composition of Soja Bean Oil.** WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1922, 44, 2947—2952).—The sample of soja bean oil examined had  $d_4^{20}$  0.9203;  $n_D^{20}$  1.4736; iodine number (Hanus) 128.0; saponification number, 189.5; acid number, 0.5; acetyl number, 17.0; Reichert-Meißl number, 0.16; Polenske number, 0.26; unsaponifiable matter, 0.6%; saturated acids, 11.5%; unsaturated acids, 83.5%. Detailed analysis showed its composition to be as follows: Glycerides of linolenic acid 2.3%, of linolic acid 51.5%, of oleic acid 33.4%, of palmitic acid 6.8%, of stearic acid 4.4%, of arachidic acid 0.7%, and of lignoceric acid 0.1%, and 0.6% of unsaponifiable matter. Total 99.8%.

W. G.

**The Chemical Composition of Sunflower-seed Oil.** GEORGE S. JAMIESON and WALTER F. BAUGHMAN (*J. Amer. Chem. Soc.*, 1922, 44, 2952—2957).—The sample of sunflower-seed oil from

south-eastern Missouri examined had  $d_{20}^{25}$  0.9193;  $n_D^{20}$  1.4736; iodine number (Hanus), 130.8; saponification number, 188.0; acid number, 2.3; acetyl number, 14.5; Reichert-Meissl number, 0.27; Polenske number, 0.25; unsaponifiable matter, 1.20%; saturated acids, 7.1%; unsaturated acids, 86.6%. Detailed analysis showed its composition to be as follows: Glycerides of oleic acid 33.4%, of linolic acid 57.5%, of palmitic acid 3.5%, of stearic acid 2.9%, of arachidic acid 0.6%, and of lignoceric acid 0.4%, and 1.2% of unsaponifiable matter. Total 99.5%.

W. G.

**The Genesis of Carbohydrates in Wheat. Presence of Lævulosans in the Stem.** H. COLIN and H. BELVAL (*Compt. rend.*, 1922, 175, 1441—1443).—Prior to the formation of the ear, the stem of the wheat plant contains only those carbohydrates coming to it from the leaf, and the ratio of reducing sugars to sucrose is much greater in it than in the leaf. From the month of June, however, as soon as the corn has shot, a change occurs. After the sugars have been extracted by alcohol from the stem a residue remains which, on hydrolysis with acid, gives a large amount of lævulose and at the time of ripening the carbohydrates of the stem consist of sucrose and lævulosans.

W. G.

**Bird-lime. III.** YUSHICHI NISHIZAWA (*J. Chem. Soc. Japan*, 1922, 43, 810—817; cf. A., 1921, i, 760; 1922, i, 652).—The decomposition products of white bird-lime have been studied. A mixture of powdered calcium oxide and bird-lime was subjected to dry distillation at the ordinary pressure and the product was fractionated at about 48 mm. pressure, the refractive indices of the fractions being measured. The fraction distilling at 155—160°/48 mm. had the formula  $C_{14}H_{28}O$  or  $C_{15}H_{30}O$ ; it did not give an aldehydic reaction. The fraction distilling at about 155°/48 mm. absorbed 8.3 g. of ozone; the product on decomposition with boiling water gave an oily aldehydic compound, its oxime had m. p. 76°, and the semicarbazone, colourless plates, m. p. 91°. From the fraction distilling at 200—270°/5—7 mm. crystals, m. p. 82°, were obtained which gave an oxime, m. p. 58°, and semicarbazone, m. p. 170°, and proved to be identical with palmitone obtained by the distillation of calcium palmitate.

K. K.

**The Soil Solution Extracted by Lipman's Direct Pressure Method compared with 1:5 Water Extracts.** PAUL S. BURGESS (*Soil Sci.*, 1922, 14, 191—216).—Analysis of 1:5 water extracts and of the soil solution shows that if all the soil moisture be assumed to act as solvent, the soil solution contains approximately as much calcium, magnesium, and nitrate as is removed in the extract, but considerably less phosphate, potash, and sulphate. On the assumption that "unfree water" exists, the amount of calcium, magnesium, nitrate, and sulphate in the extract is about twice that in the soil solution; and phosphate and potassium are in considerably larger proportions.

A. G. P.

**The Relation of Soil Moisture to Physiological Salt Balance for Plants.** JOHN W. SHIVE (*Soil Sci.*, 1922, 14, 391—411).—Crop yields on soils at various moisture-contents and with the addition of various fertilising salt mixtures were examined. It was shown that the salt balance characteristic of high yields is not markedly affected by the moisture content, provided the osmotic pressure of added solutions is roughly the same. Only when the total concentration of the solutions added to the soil were widely different was there any serious alteration in the optimum salt balance. The effect of moisture conditions on crop yield is as great as that brought about by varied fertiliser treatment. Unfavourable moisture conditions cannot be corrected by any kind of fertiliser treatment. Fertilisers cannot be utilised efficiently by the plant unless the optimum soil moisture obtains. A. G. P.

**The Potential Acidity of Soils.** OLOF ARRHENIUS (*Soil Sci.*, 1922, 14, 223—232).—The potential acidity or buffer action of soils was shown in many cases to be correlated with the type of titration curve and with soil fertility, a high buffer capacity being usually associated with a productive soil. The lime requirement of soils may be determined from data showing the relative changes in  $pH$  values brought about by titration with alkali and acid. A. G. P.

**The Measurement of Soil Acidity by Means of Alkaline Solutions.** V. VINCENT (*Compt. rend.*, 1922, 175, 1233—1234).—Solutions of lime-water and of calcium or sodium hydrogen carbonate give inconsistent results when used for measuring soil acidity, the latter giving a lower value as the organic matter in the soil combines more completely with the lime-water, whereas the hydrogen carbonate only measures organic acids together with the acidity due to aluminium salts. It is stated that these facts afford some explanation of the physical reaction of soils to the addition of calcium compounds and that the nature of the calcium compound conditions the alkalinity of the soil water. H. J. E.

**Absorption by Colloidal and Non-colloidal Soil Constituents.** M. S. ANDERSON, W. H. FRY, P. L. GILE, H. E. MIDDLETON, and W. O. ROBINSON (*U.S. Dept. Agr. Bull.*, 1922, 1122, 1—20).—A complete separation of the colloidal matter from the finer mineral particles of the soil was not found possible and a direct determination could therefore not be made of the relative absorption in soils due to colloids and non-colloids from a fractionation of the soil into these two classes of materials. From a study of the absorptive capacities of twenty-one soil minerals powdered to definite sizes varying between 1 and 50 microns in diameter, it was calculated that except in the case of the most highly micaceous soils in which the non-colloidal absorptions might reach 10—20% of the whole soil absorption, less than 5% of the total absorption of the soil is due to the non-colloidal part. Absorption by non-colloidal constituents should therefore

not seriously affect absorptive methods for estimating the amount of colloids in soil. Minerals ground to a state of subdivision probably equal to that of the mixed soil colloids, or "ultra clays," absorb less than the average ultra clay. The average absorption of peat and synthetic inorganic gels, on the other hand, is more nearly like that of the ultra clays. The fact that soil colloids are not merely finely comminuted minerals but appear to be of quite different nature from the non-colloidal particles thus affords an explanation for the marked difference in the absorptive capacities of these two classes of soil materials. CHEMICAL ABSTRACTS.

**Influence of the Calcium-Magnesium Ratio on Soils under Continuous Cultivation.** H. H. HILL (*Virginia Agr. Exp. Sta., Tech. Bull.*, 1922, 24, 1—15).—Continuous cropping of a loam soil with maize was found to change the ratio of calcium to magnesium in the soil from about 1:1 to 1:2. Good results were obtained with equal proportions of magnesium and calcium, but when magnesium was in excess, crop exhaustion was manifest. When acid phosphate was used alone, the calcium:magnesium ratio was not as wide as on the plots which received mixtures of acid phosphate, potassium sulphate, and sodium nitrate; potassium sulphate and sodium nitrate when applied alone exerted no appreciable effect on the retention of calcium. CHEMICAL ABSTRACTS.

**(Theoretical and Practical Principles of) Carbon Dioxide Manuring.** HENRIC LUNDEGÅRDH (*Angew. Botanik*, 1922, 4, 120—151; from *Chem. Zentr.*, 1922, iii, 1387).—The intensity of carbon dioxide assimilation by the leaves of beans and potatoes in closed cylinders in full daylight is nearly proportional to the concentration of carbon dioxide in the air up to two to four times the normal amount. Assimilation is increased even when the carbon dioxide content is further increased. From analyses of the atmosphere in the vicinity of leaves of growing crops it is shown that the proportion of carbon dioxide present and available for assimilation varies with different types of manuring by about 28%. The carbon dioxide concentration is increased by artificial fertilisers as well as by farmyard manure. It is shown that the carbon dioxide concentration at the level of assimilating leaves is controlled by the production of carbon dioxide in the soil. In the layers immediately above the soil, it is only slightly affected by wind velocity. Rain and warmth increase the production of carbon dioxide by the soil and, consequently, its assimilation by plants. G. W. R.

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## Organic Chemistry.

**The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. II. The Action of Oxygen on Methane.** T. SHERLOCK WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1923, 42, 81—86, 87—92r).—In continuation of previous work on the oxidation of ethylene (A., 1922, i, 1105), the authors have investigated the oxidation of methane, more especially as regards the effects of temperature, time of heating, catalysts, etc., on the production of formaldehyde. The results obtained indicate that a short time of heating and slow oxidation are the principal factors determining a good yield of formaldehyde. The higher the temperature the more liable formaldehyde, in a given concentration, is to decompose or oxidise. At 500°, it does not decompose rapidly if present in concentrations below 2%. At concentrations below 0.2%, formaldehyde is completely unstable at 720°. With shorter times of heating, equimolecular mixtures of methane and oxygen give the higher yields of formaldehyde; for longer times and probably also for higher temperatures, the yields are greater in the case of mixtures containing excess of hydrocarbon. In all cases, the yield of formic acid is very small. Whereas the presence of a very small amount of ammonia increases the stability of this product, no similar effect is observed with formaldehyde. The results are in agreement with the hydroxylation theory of the oxidation of methane proposed by Bone.

J. S. G. T.

**The Oxidation of Paraffin by means of Atmospheric Oxygen.** ADOLF GRÜN and E. ULBRICH (*Z. angew. Chem.*, 1923, 36, 125—126).—The yield of total and insoluble fatty acids in the oxidation of paraffin with air is very largely increased by increasing the rapidity of the air current. By increasing the current of air from 150 litres to 1200 litres per hour, other conditions being kept constant, the yield of insoluble fatty acids was increased from 36.5% to 61.7%. The yield is also dependent on the moisture content of the air, but the data obtained on this point are somewhat conflicting. The increase of yield caused by the more rapid air current is chiefly due to the more efficient stirring which occurs, but also partly to the increased volume of oxygen made available. Experiments carried out with air diluted with various proportions of carbon dioxide showed that gas mixtures containing as little as 1.3% by weight of oxygen exert a marked oxidising effect when passed through paraffin heated at 160°.

H. C. R.

**The Reaction between Ethylenic Hydrocarbons and the Grignard Reagent.** HENRY GILMAN and H. MARJORIE CRAWFORD (*J. Amer. Chem. Soc.*, 1923, 45, 554—558).—A quantitative study of the behaviour of magnesium methyl iodide towards a number of hydrocarbons having one or more ethylenic linkings in their

molecule shows that there is not an addition of the Grignard reagent to such a linking. This applies not only to the ordinary conditions but also in a case where an excess of the organo-magnesium halide was used or the ordinary ether was replaced by *n*-butyl ether as a solvent. W. G.

**Preparation and Reactions of Bromopicin.** LOUIS HUNTER (T., 1923, 123, 543—549).

**Unsaturated Residues in their Chemical and Pharmacological Relationship.** IV. JULIUS VON BRAUN and WERNER SCHIRMACHER (*Ber.*, 1923, 56, [B], 538—548).—It has been shown previously that unsaturated hydrocarbon residues are not firmly united with halogen, oxygen, sulphur, or nitrogen if the double bond is in the  $\beta\gamma$ -position with respect to these atoms. The effect of the lengthening of the hydrocarbon chain has been examined by a comparison of the stability of  $\Delta^2$ -butenyl compounds with the corresponding allyl derivatives. Somewhat unexpectedly, the butenyl compounds are found to be less stable than the allyl compounds. Pharmacologically the butenyl resemble the allyl derivatives in their action, but are somewhat less powerful.

$\Delta^2$ -Butenyl bromide is considerably more readily hydrolysed by water at 18° than is allyl bromide. The transformation of  $\Delta^2$ -butenyl bromide into *trimethyl- $\Delta^2$ -butenylammonium bromide*, a colourless, hygroscopic, crystalline mass, m. p. 165°, by trimethylamine dissolved in benzene takes place about two hundred times as rapidly as the conversion of *n*-butyl bromide into *trimethyl-n-butylammonium bromide*, m. p. 182°, under similar conditions.  $\Delta^2$ -Butenyl bromide reacts very readily with magnesium, giving an octadiene, b. p. 113—114°,  $d_4^{20}$  0.7420,  $n_D^{20}$  1.4324.  $\Delta^2$ -Butenyl bromide and magnesium phenyl bromide gives  *$\Delta^2$ -butenylbenzene*,  $C_6H_5\cdot CH_2\cdot CH:CHMe$ , a colourless liquid, b. p. 61—63°/12 mm.,  $d_4^{20}$  0.9069,  $n_D^{20}$  1.5157, the yield being 61% of that theoretically possible. Magnesium *p*-anisyl bromide and  $\Delta^2$ -butenyl bromide yield *p- $\Delta^2$ -butenylanisole*, b. p. 108—109°/12 mm.,  $d_4^{20}$  0.9715,  $n_D^{20}$  1.5229; the double bond in this substance appears to be very resistant to displacement towards the benzene nucleus. It is readily hydrogenated in methyl-alcoholic solution in the presence of palladium to *p-n*-butylanisole, a colourless liquid, b. p. 104—105°/10 mm.,  $d_4^{20}$  0.9396,  $n_D^{20}$  1.5045.

*Phenyl  $\Delta^2$ -butenyl ether*, a liquid, b. p. 95—98°/12 mm.,  $d_4^{20}$  0.969,  $n_D^{20}$  1.5187, is obtained in almost theoretical yield by the method recommended by Claisen and Eisleb (A., 1913, i, 1175) for the corresponding allyl compound. It is relatively more readily isomerised than the allyl derivative when heated, yielding *o- $\Delta^2$ -butenylphenol*, b. p. 108—112°/10.5 mm.,  $d_4^{20}$  1.0066,  $n_D^{20}$  1.5385; the latter substance gives non-crystalline benzoyl and *p*-nitrobenzoyl compounds, and is converted by methyl sulphate into *o- $\Delta^2$ -butenylanisole*, b. p. 102—105°/12 mm.,  $d_4^{20}$  0.9721,  $n_D^{20}$  1.5255. Similarly,  $\alpha$ -naphthyl  $\Delta^2$ -butenyl ether is partly isomerised when distilled in a vacuum to 2- $\Delta^2$ -butenyl- $\alpha$ -naphthol,

a yellow liquid, b. p. 177—180°/12 mm. (the corresponding *methyl ether* is a colourless liquid, b. p. 164—166°/13 mm.).

$\Delta^8$ -Butenyl bromide reacts very readily with ammonium thiocyanate dissolved in alcohol, but the primarily-formed  $\Delta^8$ -*butenyl thiocyanate* becomes isomerised when distilled to the corresponding thiocarbimide, b. p. 158—159° (*phenyl- $\Delta^8$ -butenylthiocarbimide* crystallises in colourless needles, m. p. 110°).

*Methyl- $\Delta^8$ -butenylaniline* is a colourless liquid, b. p. 118—120°/14 mm., which yields a non-crystalline *hydrochloride* and *picrate* and a *methiodide*, m. p. 109°. It is readily converted by cyanogen bromide into the non-crystalline, *phenylmethylidibutenylammonium bromide* (the corresponding *chloroplatinate* is a pale yellow powder, decomp. 145°), and *phenylmethylecyanamide*, b. p. 139—140°/14 mm., m. p. 32°. *Allyl- $\Delta^8$ -butenylaniline*, prepared from  $\Delta^8$ -butenyl bromide and allylaniline, is a colourless liquid, b. p. 127—130°/12 mm., which gives a non-crystalline *hydrochloride* and *methiodide* and a *picrate*, m. p. 120°. It is converted by cautious treatment with cyanogen bromide into the non-crystalline *phenylallyldibutenylammonium bromide* (corresponding *chloroplatinate*, decomp. 109°) and *phenylallylcyanamide*, a colourless liquid, b. p. 153—155°/12 mm., which is also obtained from allylaniline and cyanogen bromide.

$\Delta^8$ -*Butenylhomocholine*,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NMe}_2\cdot\text{Br}\cdot[\text{CH}_2]_3\cdot\text{OH}$ , a colourless, very hygroscopic, crystalline mass, m. p. 52°, is readily prepared from  $\gamma$ -hydroxypropyldimethylamine and  $\Delta^8$ -butenyl bromide in benzene solution.

$\Delta^8$ -*Butenylnorcodeine* has m. p. 44° after softening at 40°. The corresponding *picrate*, m. p. 128°, and *chloroplatinate*, decomp. 198—200°, are described; the *hydrochloride* has little tendency towards crystallisation.

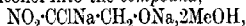
*Ethyl di- $\Delta^8$ -butenylmalonate*, b. p. 152—154°/17 mm., is prepared in 80% yield from butenyl bromide and ethyl malonate; the corresponding acid could not be caused to crystallise. The ester is converted by sodium ethoxide and carbamide into di-

$\Delta^8$ -*butenylbarbituric acid*,  $\text{CO}\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\text{C}(\text{CH}_2\cdot\text{CH}\cdot\text{CHMe})_2$ , leaflets, m. p. 109° (the *sodium salt* and the additive *product* with bromine, m. p. 195°, are described). H. W.

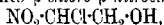
**The Function of Phosphoric Oxide in the Elimination of Water from Ethyl Alcohol and Ether.** D. BALAREFF (*J. pr. Chem.*, 1922, [ii], 368—377).—The dehydrating action of phosphoric oxide on ethyl alcohol vapour, the water in which exerts an appreciable partial pressure, or ethyl ether vapour (cf. Nef, A., 1901, i, 626) is partly catalytic and partly dependent on the formation of unstable additive products. At the ordinary temperature, ethyl alcohol gives, with phosphoric oxide, metaphosphoric acid, and the esters,  $\text{Et}_2\text{H}_2\text{P}_2\text{O}_7$ ,  $\text{EtH}_2\text{PO}_4$ ,  $\text{Et}_2\text{HPO}_4$ , and  $\text{Et}_3\text{PO}_4$ , and perhaps other compounds; with metaphosphoric acid,  $\text{EtH}_2\text{PO}_4$ . Phosphoric oxide dehydrates the esters  $\text{EtH}_2\text{PO}_4$  and  $\text{Et}_2\text{HPO}_4$ , giving a mixture of ethyl metaphosphate and pyrophosphate. W. S. N.

**Aliphatic Nitro-alcohols. The Degradation of Nitrotrimethyleneglycol.** RUDOLF WILKENDORF and MAX TRENNEL (*Ber.*, 1923, 56, [B], 611—620).—It has been shown by Henry in 1895 that "nitroisobutyglycerol,"  $\text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{OH})_3$ , is readily obtained by the condensation of nitromethane with formaldehyde under the influence of alkali hydroxides. The removal of one molecule of formaldehyde from the compound with the formation of sodionitrotrimethylene glycol,  $\text{NO}_2\cdot\text{CNa}(\text{CH}_2\cdot\text{OH})_2$ , has been effected by Schmidt and Wilkendorf (*A.*, 1919, i, 249) by means of sodium ethoxide, but the further removal of a second molecule of formaldehyde with production of  $\beta$ -nitroethyl alcohol could not be effected. If, however, the metallic atom in sodionitrotrimethylene glycol is replaced by halogen and the product is treated with sodium ethoxide,  $\beta$ -chloro- $\beta$ -nitroethyl alcohol is produced in accordance with the equation  $\text{NO}_2\cdot\text{CCl}(\text{CH}_2\cdot\text{OH})_2 + 2\text{NaOEt} = \text{NO}_2\cdot\text{CNaCl}\cdot\text{CH}_2\cdot\text{ONa} + 2\text{EtOH} + \text{H}\cdot\text{CHO}$ . If now the chloronitroethyl alcohol is liberated by addition of acid, it immediately recondenses with the aldehyde to produce the original material. It is therefore necessary to remove the formaldehyde, which is conveniently effected by treating the sodio-compound with aqueous sodium hydroxide solution and nitromethane, whereby sodionitrotrimethylene glycol is produced. The mixture is acidified and the chloronitroethyl alcohol is separated from nitrotrimethylene glycol by distillation with steam. Catalytic reduction of the former compound in the presence of palladium and pyridine yields  $\beta$ -nitroethyl alcohol.

$\beta$ -Chloro- $\beta$ -nitropropane- $\alpha\gamma$ -diol is converted by a solution of sodium in ethyl alcohol into the compound,



which is transformed into  $\beta$ -chloro- $\beta$ -nitroethyl alcohol,



b. p. 103°/15 mm. The latter substance is also obtained by the condensation of chloronitromethane with formaldehyde in the presence of saturated aqueous potassium carbonate solution. The corresponding *acetate* is a colourless, viscous liquid, b. p. 101—102°/18 mm.  $\beta\beta$ -Dichloro- $\beta$ -nitroethyl alcohol, a colourless, viscous liquid, b. p. 88—89°/12 mm. (*acetate*, b. p. 105°/28 mm.), is prepared by treating an ethereal suspension of the sodium compound prepared from  $\beta$ -chloro- $\beta$ -nitropropane- $\alpha\gamma$ -diol (see above) with a slow current of dry chlorine in the absence of light.

$\beta$ -Bromo- $\beta$ -nitropropane- $\alpha\gamma$ -diol is converted by successive treatment with an alcoholic solution of sodium ethoxide and bromonitromethane (the latter combines with the liberated formaldehyde) into the compound,  $\text{NO}_2\cdot\text{CNaBr}\cdot\text{CH}_2\cdot\text{ONa}$ , which is transformed by oxalic acid in the presence of ether into  $\beta$ -bromo- $\beta$ -nitroethyl alcohol, b. p. 113°/15 mm.; the corresponding *acetate* has b. p. 110—111°/20 mm.  $\beta\beta$ -Dibromo- $\beta$ -nitroethyl alcohol has b. p. 121°/19 mm., and yields an *acetate*, b. p. 105—106°/8 mm. Catalytic reduction of  $\beta$ -chloro-,  $\beta\beta$ -dichloro-, or  $\beta$ -bromo-nitroethyl alcohol yields  $\beta$ -nitroethyl alcohol, b. p. 102°/10 mm. Treatment of an aqueous solution of  $\beta$ -nitroethyl alcohol with hydrogen in

the presence of oxalic acid and palladised barium sulphate leads to the production of  $\beta$ -hydroxylaminoethyl alcohol oxalate, m. p. 121–123° (decomp.) after softening at 119°; the corresponding free hydroxylamino-compound could not be caused to crystallise (cf. Kühn, *Diss.*, Berlin, 1922; Lutze, *Diss.*, Berlin, 1922).

$\beta\beta$ -Dichloro- $\beta$ -nitroethyl alcohol is transformed by methylalcoholic sodium methoxide solution into sodium chloride, sodium nitrite, carbon monoxide, and nitrogen. H. W.

**Preparation of some Esters and Glycidic Derivatives of Alkylglycerols.** RAMOND DELABY (*Compt. rend.*, 1923, 176, 589–591).— $\alpha\beta$ -Dibromohydrins of alkylglycerols were obtained by the action of bromine on the corresponding alkylvinylcarbinols dissolved in twice their volume of ether.  $\alpha\beta$ -Dibromobutan- $\gamma$ -ol boils at 102–105°/13 mm.,  $d_4^{20}$  1.944,  $n_D^{23}$  1.5405.  $\alpha\beta$ -Dibromopentan- $\gamma$ -ol boils at 112–115°/15 mm., and has  $d_4^{19}$  1.828,  $n_D^{20}$  1.5327.  $\alpha\beta$ -Dibromohexan- $\gamma$ -ol boils at 126–129°/13 mm., and has  $d_4^{19}$  1.724, and  $n_D^{20}$  1.5230.  $\alpha\beta$ -Dibromoheptan- $\gamma$ -ol boils at 132–133°/12 mm., and has  $d_4^{17}$  1.613 and  $n_D^{18}$  1.5191. The displacement of the hydroxyl group by a third bromine atom could only be effected by the action of phosphorus pentabromide. The resulting tribromoderivatives had the following characters:  $\alpha\beta\gamma$ -tribromobutane, b. p. 110–113°/19 mm.,  $d_4^{18}$  2.190,  $n_D^{21}$  1.5691;  $\alpha\beta\gamma$ -tribromopentane, b. p. 125–128°/21 mm.,  $d_4^{14}$  2.095,  $n_D^{18}$  1.5621;  $\alpha\beta\gamma$ -tribromohexane, b. p. 137–141°/21 mm.,  $d_4^{13}$  1.896,  $n_D^{18}$  1.5451;  $\alpha\beta\gamma$ -tribromohexane, b. p. 148–149°/27 mm.,  $d_4^{18}$  1.827,  $n_D^{18}$  1.5394. The epibromohydrins were obtained by agitating finely powdered potassium hydroxide with an ethereal solution of the bromohydrins. The *epibromohydrin* of butane- $\alpha\beta\gamma$ -triol boils at 142–144°,  $d_4^{18}$  1.468,  $n_D^{18}$  1.4685. The *epibromohydrin* of heptane- $\alpha\beta\gamma$ -triol has a pleasant anise-like odour, b. p. 202–205°, and 91°/11 mm.,  $d_4^{17}$  1.246,  $n_D^{18}$  1.4675. Butane- $\alpha\beta\gamma$ -triol and pentane- $\alpha\beta\gamma$ -triol are well characterised by their *tribenzoates*, melting at 79–80° and 99–100°, respectively. G. F. M.

**Aluminium Trialkyl Etherates.** ERICH KRAUSE and BRUNO WENDT (*Ber.*, 1923, 56, [B], 466–472).—Aluminium trialkyls have been prepared many years ago by Buckton and Odling from aluminium and mercury alkyls. In their endeavours to obtain these compounds by a more convenient process, the authors have studied the action of ethyl bromide in the presence of ethyl ether on an alloy of magnesium and aluminium containing 15.16% of the latter together with 0.24% of silicon and traces of iron and calcium under conditions similar to those usually adopted in the preparation of Grignard's reagents. When the vigorous action is completed, the ether is removed as far as possible by distillation from a water-bath and the residue is distilled under diminished pressure in an atmosphere of nitrogen, whereby the volatile aluminium compound is removed from the non-volatile magnesium derivatives. Somewhat unexpectedly, the product is found to consist of *aluminium triethyl etherate*,  $4AlEt_3 \cdot 3Et_2O$ , a colourless, mobile liquid, b. p. 112°/16 mm., which can be preserved indefinitely

in a sealed tube even if exposed to light. It decomposes very rapidly on exposure to air, but does not generally become spontaneously inflamed; it reacts explosively with water. It has b. p.  $216-218^{\circ}$ /atmospheric pressure (very slight decomp.). The composition of the product is given with some reserve owing to the exceptional experimental difficulties encountered in its analysis but the presence of ethyl ether in the product is placed beyond doubt by its actual isolation by the cautious decomposition of the etherate with water vapour and by the synthesis of the etherate from ether-free aluminium triethyl (prepared from aluminium and mercury ethyl) and ether. The etherate is more conveniently prepared in considerable quantity by the action of sublimed aluminium chloride on a solution of magnesium ethyl bromide in ether; as thus prepared, it has b. p.  $112^{\circ}/16$  mm.,  $110.5^{\circ}/13.5$  mm.,  $d_{4}^{20}$  (vac.)  $0.8200$ ,  $n_{D}^{20}$   $1.43433$ ,  $n_{D}^{25}$   $1.43700$ ,  $n_{D}^{30}$   $1.44349$ ,  $n_{H}^{20}$   $1.44884$ .

Aluminium trimethyl etherate,  $4AlMe_3 \cdot 3Et_2O$ , has b. p.  $68^{\circ}/15$  mm., and, in contrast to the ether-free compound, cannot be caused to solidify. It almost invariably inflames spontaneously on exposure to air.

Aluminium tri-n-propyl etherate,  $4AlPr_3 \cdot 3Et_2O$ , has b. p.  $135^{\circ}/18$  mm. H. W.

**Acceleration of the Hydrolysis of  $\beta\beta'$ -Dichlorodiethyl Sulphide by Alkaline Colloidal Solutions.** ROBERT E. WILSON, EVERETT W. FULLER, and MILTON O. SCHUR (*J. Amer. Chem. Soc.*, 1922, **44**, 2762—2783).— $\beta\beta'$ -Dichlorodiethyl sulphide may be completely hydrolysed by a colloidal solution of 3% of sulphonated maize oil and 2% of sodium carbonate in thirty-five minutes at  $85^{\circ}$ . The action consists in the acceleration of the rate of solution of the gas per unit area of interface. This process was used during the war in the field laundries to effect the rapid and complete removal of "mustard gas" from contaminated clothing. J. F. S.

**Action of Methyl Sulphate and Potassium Methyl Sulphate on Monocarboxylic Acids in the Absence of Water.** L. J. SIMON (*Compt. rend.*, 1923, **176**, 583—586).—Methyl sulphate and potassium methyl sulphate can in certain cases be advantageously employed for the preparation of methyl esters by direct action on the free acids themselves in absence of water according to the equations:  $CH_3 \cdot CO_2H + Me_2SO_4 = MeHSO_4 + CH_3 \cdot CO_2Me$ , and  $CH_3 \cdot CO_2H + MeHSO_4 = H_2SO_4 + CH_3 \cdot CO_2Me$ . Thus with acetic acid the first reaction occurs on heating with somewhat more than 1 mol. of methyl sulphate at  $120^{\circ}$ , and on raising the temperature to  $200^{\circ}$  when the first reaction is nearly over, the second takes place with very slight decomposition into sulphur dioxide, etc. The yield of methyl acetate exceeds 80% of the theory. Similar results were obtained with mono-, di-, and tri-chloroacetic acids, butyric acid, etc. Benzoic acid gave a smaller yield of something over 50% of the theory. The action of potassium methyl sulphate on acetic acid at about  $200^{\circ}$  gave a 70% yield of methyl acetate, and

on benzoic acid the same yield of methyl benzoate as was obtained with methyl sulphate.

G. F. M.

**Polynuclear Acetato- and Similar Kations of Barium and of Cerium.** R. WEINLAND and ALFRED HENRICHSSEN (*Ber.*, 1923, 56, [B], 528—538).—It has been shown previously by Weinland and Stroh (A., 1922, i, 981) that lead forms polynuclear kations with acetic acid. Similar salts of barium and cerium are now described, in some of which the acetato-complex is replaced by other residues. The barium acetato-compounds all appear to contain the same dibariumdiacetato-complex,  $[\text{Ba} \langle \text{CH}_3\text{CO}_2 \rangle_2 \text{Ba}]$ .

The following individual compounds are described: *Dibariumdiacetato-perchlorate acetate*,  $[\text{Ba}_2(\text{OAc})_2] \text{OAc} / \text{ClO}_4$ , transparent, rectangular plates, obtained from barium acetate and perchloric acid or sodium perchlorate in aqueous solution (the latter mode of formation appears to indicate that the dibariumdiacetato-kation is present in barium acetate); *Dibariumdiacetato-diperchlorate*,  $[\text{Ba}_2(\text{OAc})_2](\text{ClO}_4)_2 \cdot 2\text{AcOH}$ , large, transparent prisms, from barium acetate and perchloric acid in glacial acetic acid solution; *dibariumdiacetato-picrate heptahydrate*, yellow, slender rods; *dibariumdiacetato-chlorate acetate*,  $[\text{Ba}_2(\text{OAc})_2] \text{OAc} / \text{ClO}_3$ , transparent rhombohedra, from barium acetate and sodium chlorate.

The following salts contain the analogous dibariumdiformato-kation: the *nitrate*,  $[\text{Ba}_2(\text{HCO}_2)_2]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , large, hexagonal pyramids, obtained from barium formate and nitric acid in aqueous solution; the *perchlorate formate*,  $[\text{Ba}_2(\text{HCO}_2)_2] \text{ClO}_4 / \text{HCO}_2 \cdot \text{H}_2\text{O}$ , lustrous cubes, prepared by the spontaneous evaporation of an aqueous solution of barium formate and perchloric acid; the *picrate*,  $[\text{Ba}_2(\text{HCO}_2)_2][\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2 \cdot 4\text{H}_2\text{O}$ , dark yellow prisms; the *ferricyanide potassium formate*,  $[\text{Ba}_2(\text{HCO}_2)_2][\text{Fe}(\text{CN})_6]_2 \cdot 2\text{HCO}_2\text{K} \cdot 8\text{H}_2\text{O}$ , dark red crystals, from barium formate and potassium ferricyanide; the *ferricyanide*,  $[\text{Ba}_2(\text{HCO}_2)_2][\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$ , small, dark red plates, from barium formate and sodium ferricyanide; the *cobalticyanide potassium formate*,  $[\text{Ba}_2(\text{HCO}_2)_2][\text{Co}(\text{CN})_6]_2 \cdot 2\text{HCO}_2\text{K} \cdot 8\text{H}_2\text{O}$ , pale yellow crystals; the *nitroprusside*,

$[\text{Ba}_2(\text{HCO}_2)_2][\text{Fe}(\text{CN})_5\text{NO}] \cdot 6\text{H}_2\text{O}$ , aggregates of reddish-brown leaflets.

Similar salts of cerium are described which appear to contain the triceriumtriacetato-kation. They are prepared by the action of the requisite acid on a solution of cerium acetate. Unlike the dibariumdiacetato-compounds which in certain cases can be obtained from neutral solution, the cerium compounds are only produced in a strongly acid medium. The following salts are described:

The *perchlorate acetate*,  $[\text{Ce}_3(\text{OAc})_3] \text{ClO}_4 / (\text{OAc})_4 \cdot 12\text{H}_2\text{O}$ , long, slender, colourless rods; the *picrate acetate*,  $[\text{Ce}_3(\text{OAc})_3][\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_3 \cdot 3\text{H}_2\text{O}$ , orange-red, rectangular plates; the *nitrate*,  $[\text{Ce}_3(\text{OAc})_3](\text{NO}_3)_6 \cdot 13\text{H}_2\text{O}$ .

pale pink, hexagonal plates which possibly owe their colour to traces of other rare earths; the *chromate*,  $[\text{Ce}_3(\text{OAc})_3](\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ , a yellowish-brown, microcrystalline powder; the *chloride acetate*,  $2[\text{Ce}_3(\text{OAc})_3]_{\text{OAc}}^{\text{Cl}_2} \cdot \text{Ce}(\text{OAc})_3 \cdot 28\text{H}_2\text{O}$ , colourless crystals. H. W.

**Chloroiodoacetic Acid.** HOLLAND CROMPTON and KATE MYFANWY CARTER (T., 1923, 123, 576–577).

**Trifluoroacetic Acid.** FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 343–370).—*p*-Aminobenzotrifluoride, on prolonged heating with chromic acid mixture, gives *trifluoroacetic acid* (70% of the theoretical quantity), which may be distilled over with water, and *hexa- $\alpha$ -fluoro-m-azotoluene*,  $\text{N}_2(\text{C}_6\text{H}_4\text{CF}_3)_2$ , orange needles, m. p.  $82.3^\circ$ , b. p.  $282^\circ$ , very volatile with steam. These two substances appear to form a compound, which is readily decomposed by sodium hydroxide. In the first stages of the oxidation (or, using permanganate), a brown, amorphous, sparingly soluble substance is formed, possibly a *quinonedianilide* of the formula  $\text{CF}_3\text{C}_6\text{H}_2\text{O}(\text{NH}\cdot\text{C}_6\text{H}_3\text{CF}_3)_2$ . Trifluoroacetic acid, obtained by distilling the sodium salt with sulphuric acid, forms rhombic plates, m. p.  $-15.25^\circ$  to  $-15.28^\circ$ , b. p.  $72.4$ – $72.5^\circ$ ,  $d^{20}_4$  1.53514, fumes in the air, has a vesicant action, and dissolves in water with evolution of heat. It forms a constant boiling mixture with water, b. p.  $105.46^\circ$ , 79.4% of acid. Degrees of dissociation for  $v=32$ , 64, and 128 are respectively 0.943, 0.966, and 0.979, giving a dissociation constant (100 *k*) of about 50. The sodium, potassium, ammonium, barium, and silver salts are described (cf. *Mem. Acad. roy. Belg.* [8vo collection], 1894–5, 51, and A., 1921, ii, 261). Trifluoroacetates give no fluoroform, and very little oxalic acid, when heated with sodium hydroxide (cf. A., 1906, i, 478).

*Ethyl trifluoroacetate*, obtained from sodium trifluoroacetate, alcohol, and sulphuric acid, has b. p.  $61.7^\circ/761$  mm.,  $d^{20}_4$  1.19529,  $n^{16}_D$  1.30783,  $n^{16}_B$  1.31237 and  $n^{16}_Y$  1.31527.

*Hexafluoroacetic anhydride*, from phosphoric oxide and trifluoroacetic acid, has m. p.  $-65^\circ$ , b. p.  $39.5$ – $40.1^\circ$ ; vapour non-associated. *Trifluoroacetamide*, leaflets, m. p.  $74.8^\circ$ , b. p.  $162.5^\circ$ , from the ethyl ester and ammonia, is volatile at ordinary temperatures. *Trifluoroacetoneitrile*, from the amide and phosphoric oxide, boils at about  $-61^\circ$ . Trifluoroacetic acid and aniline, when heated together at  $170^\circ$  give, besides *trifluoroacetanilide*, m. p.  $87.64^\circ$ , b. p.  $220$ – $225^\circ$ , a little fluoroform (cf. A., 1906, i, 159).

Sodium trifluoroacetate begins to decompose at  $205^\circ$ , giving *trifluoroacetyl fluoride*, b. p. about  $-59^\circ$ , together with some anhydride.

The paper concludes with a useful summary of the physical properties of various fluoro-derivatives of acetic acid, as compared with those of the corresponding chloro-derivatives. E. E. T.

**The Nature of Subsidiary Valency. XXVI. Complex Compounds with Sulphur Dioxide.** FRITZ EPHRAIM and CLARA AELLIG (*Helv. Chim. Acta*, 1923, 6, 37–53).—The extent

to which the alkali metal salts of fatty acids will form additive compounds with sulphur dioxide was studied using lithium, sodium, potassium, rubidium, and caesium salts of the normal fatty acids from formic to valeric, and, in addition, the benzoates. Gaseous sulphur dioxide was taken up very slowly by the salts, and the most satisfactory method of investigation was to mix the anhydrous salt with liquid sulphur dioxide and allow the excess to evaporate. The lithium salts did not form compounds. Of the formates, the sodium salt formed no compound, the potassium salt took up about  $\frac{1}{2}\text{SO}_2$  and the rubidium and caesium salt each about  $1\text{SO}_2$ . The remaining salts, including the benzoates, combined with approximately 1 mol. of sulphur dioxide. The sodium salt compounds are the least stable and gradually lose their combined sulphur dioxide in the course of a few months at the ordinary temperature. The potassium, rubidium, and caesium salts are comparatively stable up to  $70^\circ$ . At this temperature not merely loss of sulphur dioxide but more extensive decomposition takes place, and in the case of the formates free sulphur is formed. The additive compounds are white or faintly coloured with the exception of the formates, which are orange, resembling the compounds of alkali iodides with sulphur dioxide.

An investigation into the cause of the yellow colour of sodium hydrogen sulphite solutions showed that the colour is a characteristic property of the solution and not due to impurity. The colour was always obtained, using the purest materials, when sodium, potassium, or ammonium hydroxide solutions, or the solutions of their carbonates, sulphites, formates, and acetates were saturated with sulphur dioxide. To a less extent, the colour was obtained with solutions of calcium hydroxide and zinc acetate, but not with those of the chlorides, sulphates, and nitrates of the alkali metals nor with hydroxides of the alkaline-earth metals (except calcium), magnesium, or cadmium. The colour reaches its maximum when 5*N*-solutions of alkali hydroxides are saturated with sulphur dioxide, and is not perceptible below 0.5*N*. Spectroscopically, it is very similar to a dilute chromate solution. On dilution it does not follow Beer's law, but rapidly disappears. The colour may be due to the formation of complexes of the type of  $\text{KI}_4\text{SO}_2$  which in solution gives a colour three hundred times as intense as that of sodium hydrogen sulphite at the same concentration. There is insufficient evidence to afford a satisfactory explanation of the colour.

E. H. R.

#### Catalytic Decomposition of (Organic) Acids and Ketones.

A. MAHLER (*Caoutchouc et Gutta-percha*, 1922, 19, 473—475; from *Chem. Zentr.*, 1923, i, 38).—The decomposition of organic acids passed over a copper-aluminium catalyst at  $600\text{--}650^\circ$  is not of uniform type, since the products undergo further decomposition. Acids with six or less carbon atoms decompose almost completely with formation of gaseous products, water, and a small amount of ketones. From the higher acids liquids are produced which give on hydrogenation petroleum-like products including benzene

*m*\*

derivatives. Acetic acid gives carbon dioxide, carbon monoxide, methane, and hydrogen. *iso*Butyric acid gives hydrocarbons of the  $C_nH_{2n}$  and  $C_nH_{2n+2}$  series. Butyric acid gives the same products. Among the products from *isovaleric acid* is *isobutylene*. Benzene and toluene are found among the decomposition products of nonoic acid. Acetone gives carbon monoxide, methane, and hydrogen. Higher ketones give corresponding unsaturated compounds.

G. W. R.

**The Configuration of the Crotonic Acids.** K. VON AUWERS and H. WISSEBACH (*Ber.*, 1923, 56, [B], 715—733).—The literature of the various attempts to elucidate the configuration of the isomeric crotonic acids is exhaustively reviewed, and the various arguments which have been brought forward are criticised in detail. Since, in spite of the large amount of physical and chemical evidence which is available, it has not been possible to establish the configuration of the acids, the authors have endeavoured to decide the question by chemical means, using as starting point substances of known composition and utilising reactions which occur under mild conditions and do not immediately involve the doubly-linked carbon atoms of the acids, thus minimising the possibility of transformations and abnormal reactions.

The possibility of converting  $\gamma\gamma$ -trichlorocrotonic acid smoothly into maleic or fumaric acid has been examined. This cannot be accomplished satisfactorily by means of alkali, but fumaric acid is formed in excellent yield under the influence of sulphuric acid (60%) at 160—180°. The reaction in this state is unsuitable for configurative purposes, but, fortunately, the same change can be induced by concentrated sulphuric acid at the atmospheric temperature, although it occurs much more slowly; under these conditions, the formation of maleic acid cannot be detected. To permit valid conclusions as to the relationship of trichlorocrotonic and fumaric acids to be drawn from this result, it is, however, necessary to establish the stability of maleic acid under the experimental conditions. This acid is known to be very slightly isomerised by sulphuric acid, and in a series of experiments it is proved to be stable towards hydrogen chloride in the presence of concentrated sulphuric acid. Also, the formation of chlorosuccinic acid could not be established with certainty in any of the numerous experiments; according to the observations of previous works, it must have been produced in relatively considerable quantities if maleic acid had been formed. It is therefore regarded as established that  $\gamma\gamma$ -trichlorocrotonic acid is converted directly into fumaric acid and hence has the fumaroid configuration.

The replacement of the halogen atoms of  $\gamma\gamma$ -trichlorocrotonic acids by hydrogen has been investigated. This cannot be effected in the required manner by the action of sodium amalgam on the acid, of sodium or aluminium amalgam on its ethyl ester, or of sodium wire and moist ether on the amide. Zinc dust and acetic acid, however, convert the trichloro-acid or its ester into the di-

chloro-compounds, and the dichloro-acid is reducible by sodium amalgam to solid crotonic acid and a little butyric acid; the formation of isocrotonic acid is not observed. The possibility of molecular transformation during the reduction is discussed but regarded as highly improbable; solid crotonic acid is therefore to be regarded as the *trans*-form and isocrotonic acid as the *cis*-modification.

The configurations of the monohalogenated crotonic acids can now be deduced if it is granted that electrochemical differences in the molecules of organic compounds tend to become neutralised, and that addition of halogen if occurring in the *cis*-position is followed by loss of hydrogen halide in the same position and vice versa. Each crotonic acid must then form by addition of halogen and subsequent removal of the  $\beta$ -halogen atom as hydrogen halide an  $\alpha$ -halogeno-derivative of the stereoisomeric form. The configurations thus deduced are identical with those suggested by Michael and Pfeiffer from other considerations.

The annexed configurations (I) and (II) are ascribed to tiglic and angelic acids, respectively, since their relation to one another is very similar to that

between crotonic and isocrotonic acids (cf. Sudborough and Davies, *L.*, 1909, 95, 976).

The applicability of physical constants to the elucidation of the configuration of stereoisomeric compounds is discussed in detail. Melting point appears to be useful only in the cases of parent compounds since the mutual influence of substituents may completely alter the configurational relationship in the molecule. In the cases of density and refractive index, it does not invariably appear that the relative position of the groups is the decisive factor. Although a sufficiently large number of observations has not yet been made, it appears probable that the dissociation constant may be the most trustworthy physical datum. H. W.

**$\gamma\gamma\gamma$ -Trichlorocrotonic Acid,  $\gamma\gamma$ -Dichlorocrotonic Acid, and Maleinaldehydic Acid.** K. VON AUWERS and H. WISSEBACH (*Ber.*, 1923, 56, [B], 731—741; cf. preceding abstract).— $\gamma\gamma\gamma$ -Trichloro- $\beta$ -hydroxybutyric acid is obtained in approximately theoretical yield by the action of chloral hydrate on malonic acid in the presence of pyridine and is converted in the usual manner into  $\gamma\gamma\gamma$ -trichlorocrotonic acid.  $\gamma\gamma\gamma$ -Trichlorocrotonyl chloride, prepared conveniently by the action of thionyl chloride on the acid, is an almost colourless liquid, b. p.  $75^\circ/11$  mm., (i)  $d_4^{18}$  1.5292,  $d_4^{20}$  1.528,  $n_D^{18}$  1.51414,  $n_D^{18}$  1.51812,  $n_D^{18}$  1.52890,  $n_D^{18}$  1.53823,  $n_D^{17}$  1.5176; (ii)  $d_4^{17}$  1.5285,  $d_4^{20}$  1.525,  $n_D^{17}$  1.51395,  $n_D^{17}$  1.51798,  $n_D^{17}$  1.52881,  $n_D^{17}$  1.53830,  $n_D^{20}$  1.5167.  $\gamma\gamma\gamma$ -Trichlorocrotonamide crystallises in lustrous leaflets, m. p.  $83^\circ$ .  $\gamma\gamma\gamma$ -Trichlorocrotononitrile, obtained from the amide and phosphoric oxide, is a colourless liquid, b. p.  $74$ — $75^\circ/10$  mm., b. p.  $91^\circ/25$  mm.,  $d_4^{12}$  1.4319,  $d_4^{20}$  1.420,  $n_D^{12}$  1.50837,  $n_D^{12}$  1.51225,  $n_D^{12}$  1.52242,  $n_D^{12}$  1.53138,

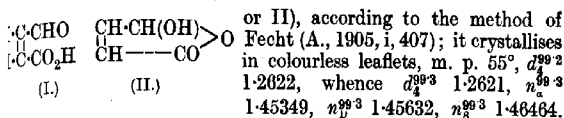
$n_D^{20}$  1.5083.  $\gamma\gamma$ -Trichlorocrotonanilide crystallises in lustrous leaflets, m. p. 162.5–163.5°.

$\gamma\gamma$ -Dichlorocrotonic acid, long, transparent, oblique prisms, m. p. 42–43°, b. p. 130°/18 mm., 123°/13 mm.,  $d_4^{20}$  1.3331, whence  $d_4^{20}$  1.3327,  $n_D^{20}$  1.45680,  $n_D^{25}$  1.45966,  $n_D^{30}$  1.46777,  $n_D^{35}$  1.47565, is readily prepared by the action of zinc dust and acetic acid on an aqueous alcoholic solution of  $\gamma\gamma$ -trichlorocrotonic acid; in consequence of the ready polymerisation of the dichloro-acid, the yields of the latter are somewhat variable but average about 60% of that theoretically possible; the reaction proceeds more smoothly if the esters are used. The ready mobility of one chlorine atom and the stability of the remaining two in the trichloro-acid is explained by Thiele's theory of partial valencies and by the assumption of residual valency of the chlorine atoms which is illus.

trated by the formula  $\begin{array}{c} \text{Cl} \\ | \\ \text{C} \\ | \\ \text{Cl} \end{array} \text{—CH=CH—C} \begin{array}{c} \text{OH} \\ | \\ \text{O} \end{array}$ .  $\gamma\gamma$ -Dichloro-

crotonic acid is converted by concentrated sulphuric acid into succinic acid in 88% yield, an aldehyde appearing to be formed intermediately. It unites readily with bromine in chloroform solution in the presence of sunlight giving  $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyric acid, lustrous leaflets, m. p. 120–121°, after previous softening. Ethyl  $\gamma\gamma$ -dichlorocrotonate, prepared by reduction of the corresponding trichloro-ester, has b. p. 91°/20 mm., 82°/12 mm.,  $d_4^{16}$  1.2323,  $d_4^{20}$  1.229,  $n_D^{16}$  1.46096,  $n_D^{18}$  1.46347,  $n_D^{16}$  1.47098,  $n_D^{16}$  1.47711,  $n_D^{20}$  1.4619. It rapidly polymerises when preserved at the atmospheric temperature. It could not be caused to react with phenylhydrazine, semicarbazide hydrochloride, hydroxylamine sulphate, or sodium iodide dissolved in acetone. Ethyl  $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyrate is an almost colourless liquid, b. p. 142–144°/14 mm., 158–159°/21 mm.,  $d_4^{22}$  1.8257,  $d_4^{20}$  1.830,  $\eta_{22}^{22}$  1.51936,  $\eta_{22}^{22}$  1.52233,  $\eta_{22}^{22}$  1.53096,  $\eta_{22}^{22}$  1.53787,  $\eta_{22}^{20}$  1.5235. Methyl  $\gamma\gamma$ -dichlorocrotonate is a colourless, mobile liquid, b. p. 77°/14 mm.,  $d_4^{17}$  1.3050,  $d_4^{20}$  1.302,  $n_D^{17}$  1.46744,  $n_D^{17}$  1.47040,  $n_D^{17}$  1.47811,  $n_D^{17}$  1.48442,  $n_D^{20}$  1.4694. Methyl  $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyrate crystallises in transparent, quadratic plates, m. p. 37° after previous softening, b. p. 145°/19 mm.  $\gamma\gamma$ -Dichlorocrotonyl chloride is an almost colourless liquid, b. p. 66–67°/12 mm.,  $d_4^{16}$  1.4429,  $d_4^{20}$  1.442,  $n_D^{16}$  1.49547,  $n_D^{16}$  1.49928,  $n_D^{16}$  1.50818,  $n_D^{16}$  1.51674,  $n_D^{20}$  1.4991.  $\gamma\gamma$ -Dichlorocrotonamide, prepared by reduction of the trichloro-compound, crystallises in needles or leaflets, m. p. 82–83°; it is converted by bromine into  $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyramide, lustrous leaflets, decomp. 162° after shrinking at 156–157°, when moderately rapidly heated.  $\gamma\gamma$ -Dichlorocrotonanilide forms long, lustrous leaflets, m. p. 83°.  $\gamma\gamma$ -Dichlorocrotononitrile is a colourless liquid with an odour of almonds, b. p. 82–83°/12 mm., 93.5–93.8°/21 mm.,  $d_4^{20}$  1.3049,  $n_D^{20}$  1.49359,  $n_D^{20}$  1.49735,  $n_D^{20}$  1.50714,  $n_D^{20}$  1.51500.

$\gamma$ -Hydroxy- $\Delta^6$ -crotonolactone is converted into maleinaldehydeic acid or 2-keto-5'-hydroxy-3:4-dihydrofuran (annexed formula, I



The optical data indicate that the cyclic form is mainly present in the molten substance. The corresponding *p*-nitrophenylhydrazone as m. p. 221° or (+EtOH), m. p. 211–212°. The aldehyde is decomposed by concentrated sulphuric acid without appearing to yield definite products; the formation of succinic acid could not be observed.

H. W.

**The Preparation and Constitution of Synthetic Fats containing a Carbohydrate Chain.** HELEN S. GILCHRIST (*Rep. Brit. Assoc.*, 1922, 357).—When  $\alpha$ -methylglucoside is heated with olive oil in the presence of sodium ethoxide, a mono-oleate of  $\alpha$ -methylglucoside is first formed, whilst in the case of mannitol di-oleate is formed. In each case, internal dehydration follows at once, the carbohydrate chain losing one molecule of water and the fatty residues remaining intact. Anhydromethylglucoside mono-oleate and mannitol di-oleate are definite chemical individuals. On methylation, they yield unstable monomethyl derivatives. When heated with acidified alcohol, they give methyl oleate together with an alkylated sugar derivative. In both cases the anhydro-ring persists during hydrolysis.

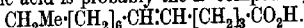
E. H. R.

**Hydrogenation and Dehydrogenation of Castor Oil and its Derivatives.** ANDRÉ BROCHET (*Compt. rend.*, 1923, 176, 513–515; cf. Mailhe, this vol., i, 88).—Castor oil is completely hydrogenated under a pressure of eleven atmospheres in the presence of reduced nickel at 112–114° in ninety minutes. The hydrogenated oil has m. p. 86° and iodine number 2. When heated in an open flask, it begins to give off hydrogen at 150°, and the volume liberated increases with rise in temperature up to about 280°. The original castor oil absorbs 70 c.c. of hydrogen per gram, but the hydrogenated oil only gives off 40 c.c. per gram. Methyl ricinoleate is hydrogenated in the same manner as castor oil and absorbs the theoretical amount of hydrogen in less than an hour at 100–105° under a pressure of twelve atmospheres.

W. G.

**A New Tetradecenoic Acid from Sperm and Dolphin Oils.** MITSUMARU TSUJIMOTO (*Chem. Umschau*, 1923, 30, 33–36).—A tetradecenoic acid,  $\text{C}_{14}\text{H}_{26}\text{O}_2$ , was isolated from sperm oil by converting the glycerides into methyl esters, separating the fraction boiling up to 180°/15 mm., brominating, and refractionating the bromo-esters, whereby a fraction boiling at 132–136°/5 mm. was obtained. This was debrominated by means of zinc and acetic acid, and saponified, non-saponifiable matter was removed by extraction with ether, and the fat acid was liberated by the addition of mineral acid. It formed a colourless liquid boiling between 190° and 200°/15 mm.,  $d_4^{15} 0.9079$ ,  $n_D^{15} 1.4566$ , iodine value 106.8. On hydrogenation it was converted into myristic acid,

and on oxidation gave a *dihydroxy-myristic acid*,  $C_{14}H_{28}(OH)_2O_2$ , m. p. 118–119°. The latter acid on oxidation with dichromate and sulphuric acid gave a reaction product from which nonoic acid was isolated. Only a very small amount of a substance which probably represented the corresponding scission product, glutaric acid, was obtained, but the results so far obtained indicate that the tetradecenoic acid is probably the  $\Delta^8$ -compound,



Tetradecenoic acid was also isolated from the low boiling fraction of the methylated sperm oil by the lead salt–light petroleum method, and from dolphin oil by the above bromination method. The yield from sperm oil was about 3% and from dolphin oil about 0.4%.

G. F. M.

**A New Substance in Birch Tar.** I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 153–156).—*Dokozanic acid*,  $C_{21}H_{42}O_2$  or  $C_{22}H_{44}O_2$ , lustrous leaflets, m. p. 72°, is found to the extent of 0.4% in birch tar; it is a fatty acid, similar in appearance and properties to stearic acid. The silver and sodium salts are prepared and described. The product of oxidation with nitric acid is an acidic substance, m. p. 67°, of the formula  $C_{22}H_{44}O_3$ , and is probably a hydroxy acid.

R. T.

**Pyruvic Acid from Lactic Acid.** J. G. SMULL and P. SUBROW (*Chem. and Met. Eng.*, 1923, 28, 357–358).—By electrolytic oxidation of lactic acid in acid, alkaline, or neutral electrolytes in a divided cell it was found that pyruvic acid was not formed when a platinum anode was used unless substances were present which removed the pyruvic acid immediately from the sphere of oxidation. Better yields were obtained by the use of a lead anode and an alkaline anolyte, but the efficiency of the process is low (cf. *J.S.C.I.*, 1923, April).

A. R. P.

**Inorganic Complex Salts. II. Erdmann's Salt and its Derivatives.** WILLIAM THOMAS (*T.*, 1923, 123, 617–619).

**Complex Metallic Ammines. VIII. The Introduction of Di- and Tri-basic Organic Acid Radicles into the Pentamminecobaltic Complex.** JAMES COOPER DUFF (*T.*, 1923, 123, 560–575).

**isoPropylmalonic Acid Derivatives and Steric Hindrance.** E. PREISWERK (*Helv. Chim. Acta*, 1923, 6, 192–198).—The effect of the *isopropyl* group on the reactivity of substituents in its proximity is often attributed to steric hindrance, but a study of the influence of the group in three compounds, ethyl *isopropyl*malonate, ethyl *isopropyl*cyanoacetate [ethyl  $\alpha$ -cyano- $\beta$ -methylbutyrate], and *isopropyl*barbituric acid, proves that this explanation does not always hold. In each of these cases the carbon atom to which the *isopropyl* group is attached carries a reactive hydrogen atom, which can, in general, be substituted by an alkyl group. Ethyl *isopropyl*malonate cannot be alkylated at all,

although the corresponding ethylmalonate and *n*-propylmalonate can be alkylated. In the case of the derivatives of ethyl cyanoacetate, the *isopropyl* derivative can be alkylated as readily as any other alkyl derivative. More remarkable than this is the observation that *isopropylbarbituric acid* can be alkylated more readily than either ethyl- or *n*-propyl-barbituric acid.

The ease with which these substances can be alkylated may be taken to depend on their acidity. Barbituric acid is a comparatively strong acid, stronger than acetic, and is not easily alkylated, on account of the stability of its alkali salts. The *C*-alkylated barbituric acids are less strongly acidic, especially the *isopropyl* derivative, which is weaker than acetic acid. By weakening the acidic properties, the alkyl groups facilitate alkylation.

In the case of ethyl cyanoacetate, the weakening of acidity due to the introduction of alkyl groups is unimportant. Ethyl malonate is the most feebly acidic of the substances under consideration and in its alkyl derivatives the acidity becomes so weak that the labile hydrogen atom loses its reactivity altogether. This explains why ethyl *isopropylmalonate* cannot be alkylated.

*Methylisopropylbarbituric acid*, obtained by methylating *isopropylbarbituric acid* in sodium hydroxide solution with methyl iodide, forms colourless crystals, m. p. 186–187°. *isopropylallylbarbituric acid* forms colourless crystals, m. p. 137–138°. *Diisopropylbarbituric acid* forms colourless crystals, m. p. 230° (decomp.).

E. H. R.

**Effect of Molybdic Acid and of Molybdates on the Rotatory Power of Malic Acid.** E. DARMOIS (*J. Phys. Radium*, 1923, 4, 49–70).—A historical résumé is given of the work of Gernez and others on the effect of alkali molybdates and tungstates on the rotatory powers of malic and tartaric acids. The author has investigated more especially the effect of ammonium and sodium molybdates on the rotatory power of malic acid. Solutions were prepared by adding ammonia or sodium hydroxide to aqueous solutions containing *n* gram-molecules of molybdic acid and 1 gram-molecule of malic acid, *n* ranging from 0 to 5, and the rotatory powers for  $\lambda\lambda$  5780, 5460, and 4360 Å. measured. Curves showing the relation of the rotatory power to *n*, for various concentrations of sodium hydroxide or ammonium, all possess respective maxima. The largest dextrorotatory power measured in each case corresponded with *n*=2, and characterised solutions containing 2 gram molecules of either ammonia or sodium hydroxide to 1 of malic acid. The results of Gernez indicating the existence of solutions having maxima of *lævo*- and *dextro*-rotations and the results of the present investigation are explicable on the assumption of the existence of definite compounds, the dimolybdomalates, *e.g.*,  $2\text{MoO}_3 \cdot \text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NaOH}$ , and  $2\text{MoO}_3 \cdot \text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NH}_3$ , and of molybdomalates, *e.g.*,  $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NaOH}$ . Crystals of sodium dimolybdomalate are monoclinic and exist as hemihedral enantiomorphs [ $a : b : c = 1.442 : 1 : 1.939$ ,  $\beta = 97^\circ 46'$ ]. Barium dimolybdo-

malate has been prepared in the form of well defined crystals. Values of the respective rotatory and dispersive powers are given.

J. S. G. T.

***d*-Malic Acid and the Utilisation of Ammonium Molybdomalate for the Decomposition of *r*-Malic Acid.** E. DARMOIS and J. PÉREL (*Compt. rend.*, 1923, 176, 391—394).—*r*-Ammonium molybdomalate is not deposited from its solution as such, but gives a mixture of crystals of the *d*- and *l*-salts, which may be separated mechanically. The optical rotation of these salts is of such a magnitude,  $[\alpha]_{578} \pm 220^\circ$ , that it is possible very readily to determine the purity of the resulting isomerides. The active molybdomalates may readily be converted into the active malic acids by decomposition with hydrogen sulphide in the presence of nitric acid, the malic acid being precipitated as its lead salt after filtering off the molybdenum sulphide. The lead salt is then decomposed by hydrogen sulphide. The preparation of *d*-malic acid from the natural *l*-acid by the Walden inversion gives a mixture of 75% of the *d*-acid and 25% of the *l*-acid, partial racemisation occurring during the inversion.

W. G.

**The Formation of Derivatives of Oxalacetic Acid from Tartaric Acid.** FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES (*T.*, 1923, 123, 663—669).

**Complex Aluminium Salts of Aliphatic Hydroxy-acids.** OSKAR GOLDMAN (*Biochem. Z.*, 1922, 133, 459—468).—The following salts of aluminium and an organic acid have been obtained: aluminium hydrogen tartrate,  $\text{Al}(\text{C}_4\text{H}_5\text{O}_6)_3$ ; ammonium hydrogen aluminotartrate,  $\text{C}_6\text{H}_{15}\text{O}_{12}\text{N}_2\text{Al}$ ; aluminotartaric acid, potassium aluminotartrate,  $\text{C}_8\text{H}_7\text{O}_{12}\text{K}_2\text{Al}$ ; sodium aluminotartrate,  $\text{C}_{12}\text{H}_9\text{O}_{15}\text{Na}_6\text{Al}$ ; an aluminium mucate,  $\text{C}_6\text{H}_7\text{O}_8\text{Al}$ ; ammonium aluminomucate,  $\text{C}_6\text{H}_{13}\text{O}_8\text{N}_2\text{Al}$ ; sodium aluminomucate,  $\text{C}_6\text{H}_5\text{O}_8\text{Na}_2\text{Al}$ . Constitutional formulæ are suggested.

W. O. K.

**Preparation of Formaldehyde.** P. BOBROV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 130—136).—The yields of formaldehyde obtained by passing a mixture of methyl alcohol vapour and air through a heated tube containing copper gauze spirals as catalyst are usually 37—42% of theory. By using instead of spirals copper gauze disks packed perpendicularly to the axis of the tube, the yields were increased to 67.6—71.6% of theory. The presence of acetone up to 4% in the spirit does not materially affect the reaction. The use of copper, gold, and silver finely distributed on asbestos, as catalysts, in conjunction with the copper disks, is tried, using spirit mixed with acetone, the amount of the latter being gradually increased to 11%. Under these conditions, copper catalyst gives yields of 70.04—72.4%, gold gives 72.79%, and silver 77.73% of the theoretical. Variations in the temperature of the alcohol vapour affect the yields less than when copper disks alone are used. On the other hand, gold and silver soon lose their catalytic power, probably owing to their relative volatility in these circumstances, which gives rise, eventually, to the formation of a

metallic mirror in the tube. Pure methyl alcohol with silver catalyst gives yields of 89.5%. The formaldehyde thus obtained, however, almost immediately polymerises to a hard, white solid, which condenses in the cooler parts of the tube, blocking it, so that the process cannot continue to the end.

R. T.

**Catalysis in the Preparation of Acetal.** HOMER ADKINS and BRYNJULV H. NISSEN (*J. Amer. Chem. Soc.*, 1922, 44, 2749—2755).—Calcium, lithium, magnesium, cerium, ammonium, manganese, and zinc chlorides, calcium nitrate, calcium bromide, copper sulphate, sodium and lithium iodides act as true catalysts and not merely as dehydrating agents in the preparation of acetal from alcohol and acetaldehyde. Acetal is best prepared by placing 200 g. of anhydrous calcium chloride and 1050 g. of 95% alcohol in a 4-litre bottle and cooling to 8° or less. Five hundred g. of cold acetaldehyde are poured slowly down the inside wall of the bottle to form a layer on the alcohol. The bottle is closed and shaken intermittently for twelve hours. After settling, the clear upper layer is separated and washed three times with water, allowed to settle, dried, fractionated, etc. Following the procedure fully detailed in the paper, a total yield of 64% can be obtained. The equilibrium point of the equation  $\text{CH}_3\cdot\text{CHO} + 2\text{EtOH} \rightleftharpoons \text{CH}_3\cdot\text{CH}(\text{OEt})_2 + \text{H}_2\text{O}$  in the presence of calcium chloride lies at 76% of acetal. Acetal has  $d_4^{20}$  0.8254,  $d_{15}^{15}$  0.8334;  $n_D^{25}$  1.3682. Its vapour pressure and solubility in water and alcohol have been determined over a wide range of temperature. The following values of the vapour pressure are recorded: 33°, 52 mm.; 52.8°, 121 mm.; 62°, 178 mm.; 71°, 244 mm.; 81.7°, 365 mm.; 90.5°, 499 mm.; 95.1°, 586 mm.; 101.2°, 720 mm.; 103°, 745 mm., and 104.2°, 760 mm.

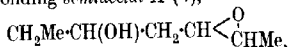
J. F. S.

**Synthesis of  $\alpha$ -Dihydroxyhexaldehyde and its Methyl Semiactal.** BURCKHARDT HELFERICH and ARNO RUSSE (*Ber.*, 1923, 56, [B], 759—766).—The synthesis of the aldehyde is described. The main interest of the work lies in the observation that the presence of two hydroxy-groups in the  $\alpha$ - and  $\gamma$ -positions of an aldehyde is sufficient for the production of two isomeric semi-acetals; under the same or similar conditions, this does not appear to be the case with  $\gamma$ -hydroxyaldehydes.

$\alpha$ -Diketoheptaldehydediethylacetal,  $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OEt})_2$ , is prepared by the action of sodium ethoxide on a mixture of diethoxyacetic ester and methyl ethyl ketone. It is a colourless, mobile liquid, b. p. 110—116°/10 mm.,  $d_4^{18}$  1.0102,  $n_D^{18}$  1.4505; the copper salt,  $\text{C}_{20}\text{H}_{34}\text{O}_8\text{Cu}$ , m. p. 115°, is described. When reduced by sodium amalgam, the aldehyde combines with only one molecular proportion of water, yielding hydroxyketo- $\alpha$ -hexaldehydediethylacetal, a viscous, pale yellow liquid, b. p. 110—120°/3.5 mm.,  $d_4^{18}$  1.0040,  $n_D^{18}$  1.4401.

Methyl dimethoxyacetate, a mobile, colourless liquid, b. p. 61—64°/12 mm.,  $d_4^{18}$  1.0962,  $n_D^{18}$  1.4045, is prepared by the action of methyl-alcoholic sodium methoxide on potassium dichloroacetate

followed by esterification of the product with methyl-alcoholic hydrogen chloride. It condenses with methyl ethyl ketone in the presence of sodium methoxide to give  $\alpha$ -diketo-n-hexaldehydedimethylacetal, a colourless, mobile liquid, b. p. 100–106°/11 mm.,  $d_4^{20}$  1.0660,  $n_D^{20}$  1.4574, which yields a dark blue monohydrated copper salt, m. p. 72°, and a dark green, anhydrous copper compound, m. p. 78°. It is reduced by sodium amalgam in alkaline solution in the presence of ammonium chloride to  $\alpha$ -dihydroxy-n-hexaldehydedimethylacetal,  $\text{CH}_3\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OMe})_2$ , a pale yellow, viscous liquid, b. p. 112–120°/3 mm.,  $d_4^{21}$  1.0407,  $n_D^{18}$  1.4460, which is hydrolysed by N/10-sulphuric acid at the atmospheric temperature to  $\alpha$ -dihydroxy-n-hexaldehyde, a pale yellow, moderately mobile liquid, b. p. 95–107.5°/0.5 mm.,  $d_4^{20.5}$  1.0927,  $n_D^{18.5}$  1.4564; the aldehyde yields amorphous products with phenylhydrazine or its p-nitro-derivative. The di-methylacetal is transformed by well-cooled, methyl-alcoholic hydrogen chloride (1%) into the corresponding semiacetal A (?),



a colourless, mobile liquid, b. p. 103–109.5°/12 mm.,  $d_4^{22.5}$  1.0510,  $n_D^{20.7}$  1.4375, and by methyl-alcoholic hydrogen chloride (0.25%) at 100° into the semiacetal B (?),  $\text{CH}_3\text{Me}\cdot\text{CH} < \begin{matrix} \text{O} \\ \text{CH}\cdot\text{OMe} \\ \text{CH}_2\cdot\text{CH}\cdot\text{OH} \end{matrix}$ , a mobile, colourless liquid, b. p. 102–115°/13–15 mm.,  $d_4^{20}$  1.0246,  $n_D^{20.6}$  1.4379. The isomerides differ from one another to some extent in odour, taste, and solubility in water, but mainly in the differing rate of hydrolysis by N/100-sulphuric acid. They are not hydrolysed by  $\alpha$ -glucosidase from yeast or by emulsin. H. W.

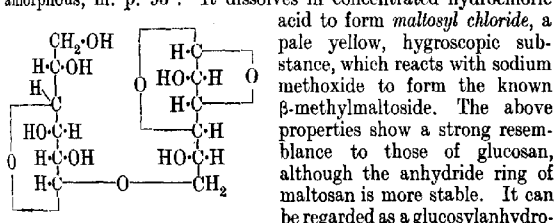
**The Hydration of Dialkylethinylcarbinols and the Preparation of  $\alpha$ -Hydroxymethyl Ketones.** RENÉ LOCQUIN and SUNG WOUSSENG (*Compt. rend.*, 1923, 176, 516–518).—The method of preparing methyl  $\alpha$ -hydroxyisopropyl ketone from methylbutinenol by the action of mercuric sulphate in dilute sulphuric acid (cf. Scheibler and Fischer, A., 1922, i, 1108), is generally applicable for the preparation of such methyl  $\alpha$ -hydroxyalkyl ketones from dialkylethinylcarbinols. The following new ketones have been prepared in this way.  $\gamma$ -Ethylpentane- $\gamma$ -ol- $\beta$ -one,  $\text{OH}\cdot\text{CET}_2\cdot\text{COMe}$ , b. p. 56–57°/13 mm., and 163–165°,  $d_4^{21}$  0.9353,  $n_D^{21}$  1.4303, giving an oxime, b. p. 116–118°, a semicarbazone, m. p. 155–156°, and an acetate, b. p. 87–90°, the semicarbazone of which has m. p. 145–146°.  $\gamma$ -Propylhexane- $\gamma$ -ol- $\beta$ -one,  $\text{OH}\cdot\text{CPr}_2\cdot\text{COMe}$ , b. p. 86–88°/14 mm., and 195°,  $d_4^{21}$  0.9124,  $n_D^{21}$  1.4343, giving an oxime, b. p. 134–135°/11 mm., m. p. 67°, a semicarbazone, m. p. 163°, and an acetate, b. p. 107–109°/13 mm.  $\beta\beta$ -Trimethylpentane- $\gamma$ -ol- $\delta$ -one,  $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{COMe}$ , b. p. 70–72°/14 mm., and 177°,  $d_4^{21}$  0.9388,  $n_D^{21}$  1.4442, giving an oxime, b. p. 124°/12 mm., m. p. 67–68°, and a semicarbazone, m. p. 193–194°.  $\gamma$ -Nonylbutane- $\gamma$ -ol- $\beta$ -one,  $\text{C}_8\text{H}_{17}\cdot\text{CMe}(\text{OH})\cdot\text{COMe}$ , b. p. 146–147°/12 mm.,  $d_4^{21}$  0.8941,  $n_D^{21}$  1.4472, giving a semicarbazone, m. p. 131–132°. 1-Acetylcyclohexan-1-ol, b. p. 91°/11 mm.,  $d_4^{21}$  1.1033,

$n_D^{20}$  1.4726, giving an *oxime*, b. p. 146–147°/11 mm., m. p. 94–95°, and a *semicarbazone*, m. p. 217°. W. G.

**Researches on Residual Affinity and Co-ordination. XV. Interactions of Acetylpropionylmethane and the Tetrachlorides of Selenium and Tellurium.** GILBERT T. MORGAN and HARRY GORDON REEVES (T., 1923, 123, 444–452).

**The Influence of Dextrins on the Crystallisation of Maltose.** L. DE HOOP and M. J. VAN TUSSENBROCK (*Biochem. Z.*, 1923, 135, 217–223).—In the commercial diastatic hydrolysis of starch, a maltose syrup is obtained which cannot be caused to crystallise directly. The authors have sought to discover the cause by determining the influence exerted by various substances, such as dextrins, proteins, peptones, and amino-acids on the crystallisation of pure maltose. It is found premature to attribute the lack of crystallising power of maltose syrup to dextrins. H. K.

**Maltosan.** AMÉ PICTET and ANDRÉ MARFORT (*Helv. Chim. Acta*, 1923, 6, 129–133).—When maltose is slowly heated to 160° under reduced pressure (15 mm.) it is converted into an anhydride, *maltosan*,  $C_{12}H_{20}O_{10}$ , forming a brown, amorphous powder which cannot be crystallised. It has no sharp m. p. but becomes viscous at 120° and liquid at 145–150°;  $[\alpha]_D^{20} +75.6^\circ$ . It cannot be distilled, and is not hydrated to maltose when boiled for a prolonged period with water. It reduces Fehling's solution at the boiling temperature, its reducing power being equal to that of maltose, and with phenylhydrazine it forms maltosazone. It reduces cold neutral potassium permanganate and is fermented by brewer's yeast. It forms a *hexa-acetyl* derivative,  $C_{24}H_{32}O_{16}$ , amorphous, m. p. 95°. It dissolves in concentrated hydrochloric



acid to form *maltosyl chloride*, a pale yellow, hygroscopic substance, which reacts with sodium methoxide to form the known  $\beta$ -methylmaltoside. The above properties show a strong resemblance to those of glucosan, although the anhydride ring of maltosan is more stable. It can be regarded as a glucosylanhydro-

glucose of the formula shown. Maltosan remains unchanged under conditions which cause polymerisation of the hexosans, such as heating with zinc chloride. E. H. R.

**The Preparation of Xylose from Maize Cobs.** ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (T., 1923, 123, 620–621).

**Swelling of Starch and the Coagulation of Albuminoids by Heat.** W. W. LEPESCHKIN (*Kolloid Z.*, 1923, 32, 42–44).—The swelling of starch is shown to be due to hydration with the formation of amylopectin. Every variety of starch has not its

own swelling temperature; this process is a chemical reaction and as such is dependent on the temperature. The temperature coefficient is extraordinarily high, and is estimated at  $57 \times 10^4$ — $83.9 \times 10^4$ . Similarly the coagulation of proteins is a chemical reaction and consists in the withdrawal of water from the molecule. This process is also dependent on the temperature and has a temperature coefficient of  $58 \times 10^3$ — $95.4 \times 10^3$ . These very high temperature coefficients are explained as due to the cumulative effects of the acceleration of the rate of diffusion, increased solubility, and increased velocity of the actual reactions.

J. F. S.

**The Starch-Iodine Complex. II.** L. BERZELLER (*Biochem. Z.*, 1922, 133, 502—508; cf. A., 1918, i, 101).—The compound formed between iodine and starch is considered to be an adsorption compound. Less iodine is taken up from alcohol than from water, and none from benzene or carbon tetrachloride, and this agrees with experimental results obtained with adsorbing charcoal. Measurements made of the adsorption of iodine by starch solution, by determination of the partition coefficient (between the starch solution and tetrachloroethane), or by dialysis, show that less is adsorbed than by solid starch.

W. O. K.

**The Limiting Dextrin formed by the Diastatic Degradation of Starch.** C. J. LINTNER and MAX KIRSCHNER (*Z. angew. Chem.*, 1923, 36, 119—122).—Achroodextrin II (cf. Lintner and Düll, A., 1895, i, 409), formed together with maltose by the action of diastase on starch, forms a dibenzoate and a diacetate and is attacked by neither emulsin nor *Saccharomyces Pombé*, but is converted quantitatively into dextrose by taka-diastase and completely fermented by the simultaneous action of diastase and yeast. Compounds intermediate between maltose and achroodextrin II, such as maltodextrins (cf. Brown and Millar, T., 1899, 286, 315), are not formed by the purely diastatic degradation of starch, and where they occur, as in beer, they must result from the action of maltase (cf. *J.S.C.I.*, 1923, April).

T. H. P.

**The Constitution of Polysaccharides. The Molecular Structure of Cotton Cellulose.** JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST (T., 1923, 123, 518—532).

**The Absorption of Sodium Hydroxide Solutions by Cotton.** HUBERT FRANK COWARD and LEO SPENCER (*J. Text. Inst.*, 1923, 14, T. 32—45).—In order to throw some light on the question whether mercerisation is a chemical or physical phenomenon, the authors have determined the composition of the solid phase when purified cotton is immersed in sodium hydroxide solutions of various concentrations, and when cotton so treated is subsequently washed in more dilute solutions of alkali or in water. The measurements made were the weight of the dried cotton (steam oven), the weight of the centrifuged mass (seven and a half minutes at 7000 revolutions per minute; see following abstract), and the weight of sodium hydroxide absorbed, as determined by titration. The temperature was 15—18°. The curves obtained for sodium

hydroxide absorbed, over the whole range of solubility of the alkali, are complex and give no indication of the formation of definite chemical compounds, neither are they of the form commonly found for simple adsorption. However, the ratio of alkali absorbed to water absorbed is greater than the ratio of alkali to water in the original solution, and this preferential absorption is approximately proportional to the concentration of the solution in contact with the cotton. The shape of the curves in this case also does not give direct evidence of the formation of definite compounds, but it is not inconsistent with the view that a series of compounds,  $(C_6H_{10}O_5)_m(NaOH)_n$ , is formed.

The volume of the absorbed solution has also been taken as a measure of the swelling of the hairs. It appears that swelling increases up to a limiting concentration of about 14.3% sodium hydroxide, when it remains constant, the hair having become about three times its original size. This limitation is imposed by the cuticle of the hair, since the contents are capable of even twelve-fold expansion. In the case of fabrics, the maximum swelling is much less, because of the mechanical constraints, and this, and similar phenomena connected with swelling, are discussed in the light of their practical significance in mercerising and dyeing.

J. C. W.

**The Efficacy of a Centrifuge for Removing Surface Liquids from Cotton Hairs.** HUBERT FRANK COWARD and LEO SPENCE (J. Text. Inst., 1923, 14, T. 29—32).—The centrifuge employed could be driven at 8000 revolutions per minute, or with an acceleration 2900 times that of gravity. Comparing the rates of removal of various liquids from cotton and glass wool, it is found that a few minutes' centrifuging, with an acceleration about 2000 times that of gravity, suffices to remove interfibrillar liquid down to 5 or 10% of the weight of the dry fibres, except in the case of very viscous liquids such as castor oil. Since, however, cotton retains water of the order of 50% of its weight, and sodium hydroxide solutions up to nearly 300%, under the above conditions, it follows that these liquids are held within the body of the cotton hairs to substantially the amount left after centrifuging as described. This is supported by the fact that cotton hairs swell considerably when immersed in water or sodium hydroxide solutions, but scarcely alter in liquids like alcohol or xylene.

J. C. W.

**Theory of the Solvent Action of Aqueous Solutions of Neutral Salts on Cellulose.** HERBERT E. WILLIAMS (Mem. Manchester Phil. Soc., 1921, 65, No. 12, 1—13).—The solution of cellulose in an aqueous solution of a neutral salt is independent of the chemical nature of the salt, but it is largely dependent on the physical properties of the salt solution. For such a solution to dissolve cellulose it must contain a hydrate, that is, an associated molecular complex of the salt and water. But this complex must be of such an order that it has a viscosity above a certain minimum, and a positive heat of dilution between well-defined limits. These limiting conditions will vary according to the nature of the cellulose

and the treatment which it has undergone; but for any particular cellulose the limits will be constant for all salt solutions in water.  
J. F. S.

**The Action of Acetyl Bromide on Cellulose.** LÁSZLÓ ZECHMEISTER (*Ber.*, 1923, 56, [B], 573—578; cf. Bergmann and Beck, A., 1921, i, 649; Hess, A., 1922, i, 12; Karrer, A., 1921, i, 311, 766, 768; Zechmeister, *Diss.*, Zürich, 1913).—It does not appear to be possible to convert intact or nearly intact cellulose by means of acetyl bromide into acetylbromo-derivatives. The material behaves indifferently towards the reagent, acetylation or introduction of the bromine atom only occurring to a marked extent as it passes into solution, becoming thereby considerably degraded. Hydrogen bromide and acetic acid which are invariably present in technical acetyl bromide have a very important accelerating action on the acetolysis of cellulose. If the reagent is purified by being distilled over bright calcium turnings, its attack is very greatly delayed.

By the cautious addition of water to acetyl bromide, it is possible to hydrolyse it to any desired extent; it is found that with increasing hydrolysis its action becomes increasingly energetic. The course of the change is followed by analysis of the products which can be precipitated with water, since the undissolved fibres are not appreciably affected and the soluble products are difficult to determine. In the initial stages of the change, fission of the cellulose molecule appears to be initiated by hydrogen bromide, after which the disengaged hydroxyl groups become acetylated. Hydrogen bromide is thereby liberated which further hastens the general degradation. Hand in hand with the step-wise conversion into derivatives of simpler carbohydrates there occurs a partial displacement of the acetyl groups by the bromine atom, which resembles the conversion of dextrose penta-acetate into acetylbromoglucose.

Starch is converted by technical acetyl bromide into acetobromoglucose; the yields are, however, poor, and the conversion is effected more readily by acetyl bromide and a large excess of hydrogen bromide (cf. Bergmann and Beck, *loc. cit.*). It is remarkable that pine wood is soluble without residue in technical acetyl bromide (cf. Karrer and Widmer, A., 1921, i, 771). H. W.

**[Cellulose Copper Compounds.]** KURT HESS and ERNST MESSMER (*Ber.*, 1923, 56, [B], 587—591; cf. A., 1921, i, 401; 1922, i, 988).—A reply to the recent criticisms of Traube (this vol., i, 186). H. W.

**Nature of the Swelling Process. VII. Molecular Processes during Swelling and the Heat of Swelling.** E. KNOEVENAGEL and E. VOLZ (*Koll. Chem. Beihefte*, 1923, 17, 51—71; cf. A., 1921, i, 420, 709, 710, 771; this vol., i, 17).—A continuation of previously published work. The swelling of cellulose acetate in binary mixtures of alcohol, nitrobenzene, and benzene has been investigated for a large number of binary mixtures of

various compositions. The results show that the liquid is adsorbed by the cellulose acetate in molecular proportions. The number of molecules of alcohol, benzene, or water adsorbed bears a constant relationship to the number of molecules of cellulose acetate, and where binary liquid mixtures of varying composition are used the sum of the number of molecules of each liquid taken up in the swelling is constant. The heat change occasioned by the swelling of cellulose acetate in the same binary mixtures has also been determined. The results although complicated by the nature of the process clearly indicate that the heat change has a molecular relationship.

J. F. S.

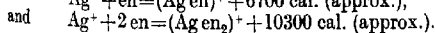
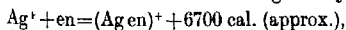
**Graphic Representation of the Decomposition of Mono-, Di-, and Tri-methylamine Gas Mixtures.** RUDOLF MICHEL (*Chem. Ztg.*, 1923, 47, 173—174).—A method is developed for the graphic representation of the thermal decomposition of the methylamines into hydrogen cyanide, ammonia, methane, hydrogen, and carbon. All the possible ways in which this may occur are summed up in the three following fundamental equations: (1)  $\text{NH}_2\text{Me} = \text{NH}_3 + \text{H}_2 + \text{C}$ ; (2)  $\text{N}(\text{CH}_3)_2 = \text{HCN} + 2\text{CH}_4$ , and (3)  $\text{N}(\text{CH}_3)_3 = \text{HCN} + 4\text{H}_2 + 2\text{C}$ , and the gas mixtures formed are represented each by a corner of a Gibbs triangle, every point within the triangle thus representing one of the possible mixtures of gases which may arise from the decomposition of a methylamine mixture. The thermochemical relationships are also expressed by means of a Gibbs triangle in a similar way.

G. F. M.

**Researches on Pseudo-bases. IV. A New Synthesis of Tertiary Amines of the Form  $\text{R}\cdot\text{CH}_2\cdot\text{NR}^1\text{R}^2$ .** GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (*T.*, 1923, 123, 532—543).

**Perhalides of Quaternary Ammonium Salts.** FREDERICK DANIEL CHATTAWAY and GEORGE HOYLE (*T.*, 1923, 123, 654—662).

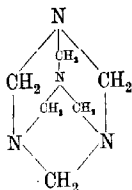
**The Complex Ions formed by Silver Salts and Ethylenediamine in Aqueous Solution.** P. JOB (*Compt. rend.*, 1923, 176, 442—445).—The silver-ion forms with ethylenediamine, in a dilute aqueous solution of the silver salt, two complex ions of the types  $\text{Ag en}_2$  and  $\text{Ag en}$ , where en represents a molecule of ethylenediamine. The second complex only exists in any appreciable quantity when the concentration of the diamine is very small. The equilibrium constants of the two ions are  $K = 6.8 \times 10^7$  and  $k = 10^5$ , respectively, at 16°. The affinities of the silver-ion for ethylenediamine are in normal solution given by



The second value coincides almost exactly with the value calculated by Bodländer (*A.*, 1904, ii, 122) for the affinity of silver for ammonia.

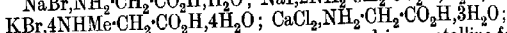
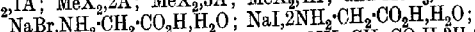
W. G.

**Crystal Structure of Hexamethylenetetramine.** ROSCOR G. DICKINSON and ALBERT L. RAYMOND (*J. Amer. Chem. Soc.*, 1923, 45, 22—29).—Crystals of hexamethylenetetramine have been examined by X-ray methods, using spectral photographs and Laue photographs. The data thus obtained have been accounted for by a structure with tetrahedral symmetry which may be regarded as built up of like molecules of  $C_6H_{12}N_4$  in parallel orientation and on a body-centred cubic lattice of edge 7.02 Å. Both the carbon



atoms and the nitrogen atoms are equivalent among themselves. This fact is not shown by any of the structural formulæ hitherto put forward for this substance, but is in keeping with the annexed formula. Two nitrogen atoms are at a distance of about 1.44 Å. from each carbon atom, and at least approximately in the direction of two vertices of a tetrahedron, which is in agreement with the accepted view of the tetrahedral nature of the carbon atom. J. F. S.

**Compounds of Normal Salts with Amino-acids and Polypeptides.** PAUL PFEIFFER (*Z. angew. Chem.*, 1923, 36, 137—138).—Compounds of the types  $MeX_n, 1A$ ;  $MeX_n, 2A$ ;  $MeX_n, 4A$ ;  $MeX_n, 1A$ ;  $MeX_n, 2A$ ;  $MeX_n, 3A$ ;  $MeX_n, 4A$ ; and  $MeX_n, 3A$  such as



and  $CaBr_2, 3NH_2 \cdot CH_2 \cdot CO_2H$  have been prepared in crystalline form and they yield clear neutral aqueous solutions. From a consideration of their solubility, optical activity, and depression of the freezing point in aqueous solution, it is concluded that these complex compounds exist even in solution. Hence it is suggested that the adsorption of salts by the more complex colloids, such as albumin, is partly due to chemical combination, and the fact that such adsorption does not occur in definite constant proportions is ascribed to the inability of the normal salt to penetrate completely into the complex albumin molecules. This chemical theory of adsorption is also considered to hold good in industrial processes such as dyeing, weighting of silk, and tanning. A. J. H.

**Synthesis of Two New Leucines.** K. KURONO (*Biochem. Z.*, 1922, 134, 434—436).— $\alpha$ -Amino- $\alpha$ -methylvaleric acid and  $\alpha$ -amino- $\alpha$ -dimethylpropionic acid have been prepared by the method of Zelinsky and Stadnikoff. The former melts in a sealed tube at 295° and forms a deep blue copper salt, readily soluble in water and in spirit.  $\alpha$ -Naphthylcarbamido- $\alpha$ -methylvaleric acid melts at 191°. The second acid melts in a sealed tube at 293° and forms a deep blue copper salt, easily soluble in water. H. K.

**A New Type of Nitrogenous Sugar Derivative.** JOHN PRYDE (*Rep. Brit. Assoc.*, 1922, 357—358).—Tetramethylglucose was oxidised to tetramethylgluconic acid, which was isolated as the lactone. When this was treated with dry ammonia in alcoholic solution, a crystalline compound was obtained which appeared to

be, not the acid amide, but an amino-lactone. When this was treated with cold alkaline hypochlorite, a crystalline substance was obtained having the composition of the expected intermediate carbimide, but also having, from its behaviour, the constitution of an internal urethane,  $\text{OMe-CH} \begin{smallmatrix} \text{CH(OMe)} \\ \text{CH-O-CO} \end{smallmatrix} \text{>NH}$ . The formation of this substance shows the stabilising effect of methyl groups in the sugar chain and is an interesting example of the conversion of a carbohydrate into a derivative in which nitrogen is present in a stable cyclic substituent.

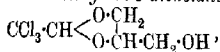
E. H. R.

**A Remarkable Occurrence of Carbamide.** EDMUND O. VON LIPPMANN (*Ber.*, 1923, 56, [B], 566—567).—A deposit observed in the blind end of a tube connected with the main steam supply of a beet-sugar factory was found to consist of nearly pure carbamide. The ammoniacal liquor of the evaporating plant was used as feed water for the boilers, and was apparently unusually rich in ammonia. Ammonium carbamate appears to have been the precursor of carbamide.

H. W.

**Urethanes from Chlorine-substituted Secondary and Tertiary Alcohols.** LESTER YODER (*J. Amer. Chem. Soc.*, 1923, 45, 475—479).—The carbamates of chlorine-substituted secondary and tertiary alcohols containing a trichloromethyl group were prepared by treating the sodium or the magnesium bromide derivative in benzene or ethereal solution with carbonyl chloride and then adding ammonia to the acid chloride thus formed. In this way were prepared *dimethyltrichloromethylcarbonyl carbamate*, m. p.  $102^{\circ}$ , *phenyltrichloromethylcarbonyl carbamate*, m. p.  $127^{\circ}$ , *dimethyltrichloromethylcarbonyl carbamate*, m. p.  $118^{\circ}$ , *dimethyldichloromethylcarbonyl carbamate*, m. p.  $122^{\circ}$ , and *methyltrichloromethylcarbonyl carbamate*, m. p.  $125^{\circ}$ .

Chloral hydrate condenses with glycerol in the presence of zinc chloride to give *2-trichloromethyl-1:3-dioxolane-4-carbinol*,

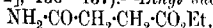


b. p.  $125\text{--}128^{\circ}/10\text{ mm.}$ , which yielded a *urethane*, m. p.  $114^{\circ}$ .

The new alkyltrichloromethyl carbamates are tasteless and odourless. Methyl- and dimethyl-trichloromethyl carbamates have quite a strong hypnotic action. The dioxolane has a marked and fleeting hypnotic effect but its urethane has practically no hypnotic effect.

W. G.

**Ethyl Succinamate.** P. P. RUBCOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, [1—2], 136—137).—*Ethyl succinamate*,



m. p.  $74\text{--}75^{\circ}$ , b. p.  $230\text{--}240^{\circ}$ , is obtained by heating the silver salt of the corresponding acid in a sealed tube for two hours at  $60\text{--}65^{\circ}$  with ethyl iodide.

R. T.

**Decomposition and Formation of Calcium Cyanamide.** VICTOR EHRLICH (*Z. Elektrochem.*, 1922, 28, 529—542).—The con-

ditions under which the decomposition and formation of calcium cyanamide occur have been experimentally investigated. It is shown that the decomposition of calcium cyanamide, which commences above  $1100^{\circ}$ , is not determined solely by the temperature. Above  $1200^{\circ}$ , calcium cyanamide sublimes, but at  $1300^{\circ}$  a re-formation of calcium carbide can be deduced from the separation of lime and carbon in the nitrolime reaction. The carbon monoxide thus produced decomposes the pure sublimed calcium cyanamide partly with the formation of lime and carbon and partly with the formation of calcium carbide. Pure calcium cyanamide sublimes at  $1300^{\circ}$  without previously melting; the addition of approximately 10% of lime reduces the melting point to  $1200^{\circ}$ , and an addition of 15% of calcium chloride reduces it to  $850-900^{\circ}$ . Calcium cyanamide, free from carbon, decomposes above  $1000^{\circ}$  with the liberation of nitrogen according to the equation  $\text{CaC} + \text{N}_2 = \text{CaCN}_2$ . Dissociation pressure measurements have been made for various temperatures; the following values are recorded:  $1000^{\circ}$ , 2.5 mm.,  $1100^{\circ}$ , 14 mm.,  $1140^{\circ}$ , 32 mm., and  $1190^{\circ}$ , 73 mm. The addition of other materials to calcium cyanamide has little effect on the dissociation pressure at temperatures below  $1200^{\circ}$ , but above this temperature, due to the rapid sublimation of the calcium cyanamide and consequent reduction of the concentration, the dissociation pressure is strongly reduced. The decomposition of calcium cyanamide takes place with a much smaller nitrogen pressure than is the case with nitrolime under the same temperature conditions. The presence of carbon, therefore, raises the dissociation pressure, very probably under the influence of the reaction  $\text{CaC}_2 = \text{CaC} + \text{C}$  which takes place from left to right below  $1100^{\circ}$  and in the opposite sense above this temperature. The process is a heterogeneous one, the course of which is determined by the constitution of the surface and the velocity of diffusion. The nitrolime reaction represented by the equation  $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$  can be regarded as made up of the two reactions indicated by equations, above. A primary formation of cyanide is unlikely. The heat change of the formation of calcium cyanamide has been calculated on the basis of the Nernst heat theorem, and the value 61400 cal. obtained. It is likely that the heat change in the formation of nitrolime does not differ much from this value but is possibly a little higher.

J. F. S.

**Action of Organometallic Derivatives of Magnesium on Nitriles.** P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 7-23).—Acetonitrile (1 mol.) reacts with ethereal magnesium methyl (ethyl) bromide (1 mol.) to give methane (ethane) (1 mol.), and, according to conditions, either diacetonitrile, or one of its condensation products (3-cyano-6-hydroxy-2:4-dimethylpyridine [cf. Moir, T., 1902, 81, 100] or 6-amino-3-cyano-2:4-dimethylpyridine [cf. von Meyer, A., 1908, i, 909]). The initial course of the reaction is to be represented thus:  $\text{CH}_3\text{CN} \rightleftharpoons \text{CH}_2\text{:CNH} \rightarrow \text{CH}_2\text{:CNMgBr} \rightarrow \text{NH:CMg-CH}_2\text{CN}$ . No acetone is formed, and special care is necessary if diacetonitrile itself is required. Two

other substances are formed: (1) a solid substance,  $C_8H_7N_3$  (?), m. p. 198–200°, converted by boiling water into ammonia and a substance of m. p. 135°; and (2) a base,  $C_7H_7N_2$  (?), m. p. 123°, giving a chloroaurate, m. p. 103°.

E. E. T.

**Action of Organometallic Derivatives of Magnesium on Nitriles.** OMER DE BOOSERÉ (*Bull. Soc. chim. Belg.*, 1923, 32, 26–51).—An investigation affording further evidence that nitriles do not always behave normally with the Grignard reagent.  $\gamma$ -Chlorobutyronitrile, when treated with an equimolecular proportion of magnesium ethyl bromide, is converted into four substances, as follows: (1) *cyclopropyl ethyl ketone* (23–25%) (cf. A., 1909, i, 226). (2) *Ethyl  $\gamma$ -chloropropyl ketone* (14–17%), colourless liquid, b. p. 182–183°/761 mm., or 77.5–78.5°/15 mm.,  $n_D^{20}$  1.4411,  $d_4^{20}$  1.0269; gives a *semicarbazone*, m. p. 98–99°; with solid potassium hydroxide gives *cyclopropyl ethyl ketone* (cf. A., 1889, 843), the latter giving the chloro-ketone when treated with hydrochloric acid. This fraction (2) also contains *cyclopropyl ethyl ketimine*, liquid, b. p. 127–128°/759 mm. (*hydrochloride*, solid, b. p. 160–170°/14–16 mm.) (cf. A., 1920, i, 485). (3) *Ethyl amyl ketone* (?). (4) Polymerides of *cyclopropane carboxylonitrile*. When, in the above reaction, two molecular proportions of Grignard reagent are used, the yields of fractions (1) and (2) become, respectively, 28–30% and 27–31%.

The interaction of magnesium ethyl bromide and ethyl  $\gamma$ -chloropropyl ketone affords as primary product the expected *diethyl- $\gamma$ -chloropropylcarbinol*, but the latter on distillation, even under diminished pressure, decomposes to give (1)  $\beta$ -ethylhexylene  $\beta$ -oxide, b. p. 145–150°,  $n_D^{20}$  1.4317,  $d_4^{20}$  0.8703, (2)  $\zeta$ -chloro- $\gamma$ -ethyl- $\Delta^1$ -hexene, b. p. 173°,  $n_D^{20}$  1.4524,  $d_4^{20}$  0.9102, and (3) an inseparable mixture (b. p. 90–105°/15 mm.), probably containing *diethyl- $\gamma$ -chloropropylcarbinol* and  $\gamma$ -*dichloro- $\gamma$ -ethylhexane* (cf. A., 1909, i, 79). The product of the interaction of magnesium ethyl bromide and ethyl  $\gamma$ -chlorobutyrate, evidently the above carbinol, decomposes, even on distillation under diminished pressure, more of the chlorohexene being produced in this case.

$\beta$ -Chlorobutyronitrile (1 mol.) and magnesium ethyl bromide (1 mol.) give rise to a mixture containing (1) the two isomeric crotononitriles (cf. A., 1922, i, 817), (2), the *trimeride* of one of these, white needles, m. p. 173–174°, b. p. 215–240°/13 mm., and (3) a small quantity of a mixture of two ketones. When 2 mols. of Grignard reagent are used, the main product is the trimeric crotononitrile.

$\alpha$ -Chlorobutyryl chloride, when added to aqueous ammonia at 0°, is converted into  $\alpha$ -chlorobutyramide, which also is formed when methyl  $\alpha$ -chlorobutyrate is digested for several hours with concentrated aqueous ammonia. The author notes that the chlorination of a mixture of butyric acid and butyryl chloride gives, besides  $\alpha$ -chlorobutyryl chloride, the *anhydride*, b. p. 125–130°/15 mm.

$\alpha$ -Chlorobutyramide, white needles, m. p. 81°, gives  $\alpha$ -chlorobutyronitrile with thionyl chloride. This nitrile, with one mole-

cular proportion of magnesium ethyl bromide, is converted into a mixture containing (1) a small quantity of an unsaturated hydrocarbon (?), b. p. 76–85°, (2) the two crotononitriles, and (3) unidentified products of higher b. p. When two molecular proportions of Grignard reagent are used, no hydrocarbon is formed and very little crotononitrile, the main product being an amine, which the author believes to be  $\gamma$ -imino- $\gamma$ -ethylhexane,  $\begin{matrix} \text{C} \\ \text{C} \end{matrix} \begin{matrix} \text{Et}_2 \\ \text{Et} \end{matrix} > \text{NH}$ .

The latter boils at 157–158°, combines with calcium chloride, forms a hydrochloride (white needles, m. p. 185–186°), gives a yellow crystalline chloroplatinate and reacts with bromine to give a *N*-bromo-derivative. A secondary product of the above reaction, of unknown constitution, boils at 118–123°/15 mm. E. E. T.

**Solubility of Prussian Blue.** MORTZ KOHN (*Monatsh.*, 1923, 43, 373–376).—Prussian Blue dissolves in solutions of the neutral oxalates of potassium, sodium, and ammonium to give greenish solutions. The interaction of ferric chloride and potassium ferrocyanide, even if an excess of one of these substances is present, does not lead to a precipitate of Prussian blue in presence of these neutral oxalates. The above green solutions, unlike those of Prussian blue in aqueous oxalic acid, are true solutions.

E. E. T.

**The Formation of Hydroxamic Acids from Keten.** CHARLES DE WITT HURD and PAUL B. COCHRAN (*J. Amer. Chem. Soc.*, 1923, 45, 515–521).—Keten will react readily with a monohydroxamic acid to form, not only a monoacetyl ester, but also a diacetyl ester. In this way, from pyromucylhydroxamic acid the authors obtained, not only the monoacetate, m. p. 94–96°, but also the diacetate, m. p. 54–55°. Similar results were obtained with diphenylacet-hydroxamic acid and benzhydroxamic acid.

An improved apparatus is described for preparing keten by the method of Schmidlin and Bergman (*A.*, 1910, i, 816), the undecomposed acetone issuing from the reaction tube being removed from contact with the keten almost as soon as it leaves the tube.

The similarity of the behaviour of keten and of phenylthiocarbimide towards monohydroxamic acids is discussed. W. G.

**Mercury Propyl and Mercury isoPropyl.** MARCEL GORET (*Bull. Sci. Pharmacol.*, 1922, 29, 297–305; from *Chem. Zentr.*, 1922, iii, 1371).—Mercury dipropyl is prepared by the action of sodium amalgam on propyl bromide in the presence of ethyl acetate. It is separated from the products of reaction by distillation in steam and subsequent fractionation; it has  $d_4^{20}$  2.046; b. p. 189°/760 mm., 82–86°/25 mm. From the residue after steam distillation mercury propyl is obtained after crystallisation from ethyl alcohol in leaflets, m. p. 135°. Mercury propyl chloride is obtained by the action of mercuric chloride on mercury propyl in alcoholic solutions; it forms white scales, m. p. 143°. Mercury propyl bromide, from the action of bromine on mercury propyl, forms leaflets, m. p. 135°. Mercury propyl iodide is crystalline, m. p. 113°. Mercury propyl acetate, from the action of acetic anhydride on mercury dipropyl or of

acetic acid on the corresponding hydroxide, is crystalline, m. p. 57–58°. *Mercury diisopropyl* has b. p. 75–77°/25 mm.,  $d_4^{20}$  2.05. *Mercury isopropyl hydroxide* is prepared by the action of moist silver oxide on one of the halides. It gives with the corresponding acids, *mercury isopropyl sulphide*, m. p. 60°; *mercury isopropyl cyanide*, m. p. 85°; *mercury isopropyl acetate*, m. p. 95°; *mercury isopropyl chloride*, needles, m. p. 97°. *Mercury isopropyl bromide* forms needles, m. p. 98°; *mercury isopropyl iodide*, leaflets, m. p. 125°.

G. W. R.

**Low Temperature Coal Tar and the Products of its Superheating.** FRANZ FISCHER (*Ber.*, 1923, 56, [B], 601–603).—In a recent communication, Schütz (this vol., i, 195) has described a low temperature tar which differs greatly from that obtained previously by the author and his co-workers (*A.*, 1917, i, 258; 1920, i, 277), in that it contains very considerable amounts of benzene and phenol. The differences cannot be attributed solely to the differing types of coal employed; it appears that the product examined by Schütz was a superheated low-temperature tar. The temperature employed (500–600°) is considerably higher than that which is actually necessary, and the structure of Schütz's retorts is such that the volatile products are necessarily exposed to the highest temperature of the furnace. Under these conditions, it has been shown previously that hydroaromatic hydrocarbons are dehydrogenated to benzene, and phenols with a long side chain are transformed into phenol and olefinic hydrocarbons. The volume of gas obtained by Schütz from each ton of coal is much greater than that usually observed in low-temperature work, and affords additional evidence of secondary decomposition. H. W.

**The Benzene Theory.** C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 82–83).—An answer to criticisms by Olivier, by Prins, and by Schoutissen (this vol., i, 195, 196) of the triangular formula suggested by the author (this vol., i, 99).

S. I. L.

**Is Kekulé's Benzene Theory Tenable?** C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 90–96).—The triangular formula and the theory of synchronous rotation put forward for benzene (this vol., i, 99) are developed and extended to pyridine, thiophene, pyrrole, quinoline, pyrazole, glyoxaline, etc.

S. I. L.

**Solubility of cyclohexane in Liquid Sulphur Dioxide.** W. F. SEYER and V. DUNBAR (*Trans. Roy. Soc. Canada*, 1922, 16, III, 307–310).—A determination of the equilibrium diagram of the system liquid sulphur dioxide–cyclohexane indicates the existence of a transition point at  $-17.0^\circ$ , corresponding with the maximum solubility of sulphur dioxide in cyclohexane, and of a eutectic point at  $-72.5^\circ$ , at which temperature the solubility of cyclohexane in liquid sulphur dioxide is very small. Above  $13.6^\circ$ , the liquids are miscible in all proportions. No evidence of the formation of compounds of the two substances, as suggested by Moore, Morrell, and Egloff (*A.*, 1918, i, 285), was obtained.

J. S. G. T.

**Trifluoromethylcyclohexane.** FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 505—530; *Bull. Soc. chim. Belg.*, 1923, 32, 70—79).—A continuation of previous work (A., 1921, i, 656). The m. p. of trifluoromethylcyclohexane is  $-103.4^{\circ}$  to  $-103.5^{\circ}$ . The group  $\cdot\text{CF}_3$  is even more resistant to reagents in this case than in the case of benzotrifluoride. Trifluoromethylcyclohexane is hydrolysed to cyclohexanecarboxylic acid only to the extent of 3% when heated at  $180^{\circ}$  with aqueous hydrobromic acid ( $d^{17} 1.768$ ) for eighty hours, in presence of silicon dioxide. Neither sodium hydroxide nor sodium amalgam affects the fluoro-compound in alcoholic solution. Bromine (1 mol.), at  $130^{\circ}$  under pressure, affords the bromo-derivative, a colourless liquid, b. p.  $177-178^{\circ}$ ,  $d^{16} 1.561$ , together with the dibromo-derivative (the main product), b. p.  $218-220^{\circ}$  (slight decomp.), or  $120-122^{\circ}/30$  mm.,  $d^{17} 1.912$ , and a little tribromo-derivative, b. p.  $260-265^{\circ}$  (slight decomp.). The introduction of a bromine atom into the cyclohexane ring in this case facilitates further substitution. An excess of bromine (under pressure, at  $170^{\circ}$ ) converts the original fluoro-compound into a mixture of 3:4- and 2:5-dibromobenzoic acids and another substance not identified. Dilute permanganate solutions have little effect on the fluoro-compound at water-bath temperatures; no toluene derivatives are formed, the change that does occur resulting in complete oxidation of the molecule.

In an attempt to prepare the hexanol from trifluoromethylbromocyclohexane, the latter was heated under pressure with an aqueous suspension of mercuric oxide, and gave rise, instead, to trifluoromethylcyclohexene, a mobile liquid, b. p.  $104.5-105.5^{\circ}$ ,  $d^{16} 1.127$ ; dibromide (?), b. p.  $219-220^{\circ}$ .

Zinc and ethyl alcohol converted trifluoromethyldibromocyclohexane into what is probably the same hexene. The product boils at  $104.7-104.9^{\circ}/762$  mm., and has  $d^{16} 1.1368$  and  $d^{18} 1.1194$ . It forms a constant boiling mixture with alcohol (b. p.  $74.4^{\circ}$ ; 57.5% of the hexene).

In the dibromo-derivative, one bromine atom is in position 3 ( $\cdot\text{CF}_3$  in 1), and the other in position 2 or 4.

Nitric acid ( $d 1.15$ ) at  $130^{\circ}$  converts trifluoromethylcyclohexane into a mononitro-derivative, but a large amount of decomposition occurs (see below). The nitro-derivative is a viscous liquid, b. p.  $224-225^{\circ}$  or  $124.5^{\circ}/30$  mm.,  $d^{16} 1.3154$ . The sodium derivative is very soluble in alcohol. Among the products of decomposition referred to were isolated trifluoroacetic, succinic, and trifluoromethyladipic acids (?); other products probably were fluoro-derivatives of  $\text{C}_6$  and  $\text{C}_7$  carboxylic acids. Similar decomposition products were obtained by heating the nitrocyclohexane with nitric acid.

E. E. T.

**The Isomeric Trinitrotoluenes.** H. BRUNSWIG (*Z. anorg. Chem.*, 1923, 36, 75—76).—A short review of the work to date on the preparation of the six isomeric trinitrotoluenes. The results of an investigation on the stability of these compounds towards heat, either alone or mixed with one-fifth of their weight of sodium

hydroxide, and on their behaviour towards sodium carbonate and lead oxide in boiling alcohol are given in tabular form with a view to supply a method for their identification, and also for their detection in the manufactured product. Their detonation temperatures, when heated alone, are all in the neighbourhood of  $100^{\circ}$  and are too close to one another to be of service. The remaining tests applied resulted as follows— $\alpha$ -Trinitrotoluene [2:4:6] (a) m. p.  $80.5^{\circ}$ . (b) Crystallises from methyl alcohol in needles. (c) With sodium carbonate in boiling alcohol, coloured dark reddish-brown without transformation into dinitrocresol; on continued boiling is converted into another dark salt. (d) With lead oxide in boiling alcohol, unaltered. (e) Detonation temperature mixed with sodium hydroxide,  $230-233^{\circ}$ .  $\beta$ -Trinitrotoluene [2:3:4] (a) m. p.  $112^{\circ}$ . (b) Needles. (c) Forms sodium dinitrotolyloxide readily. (d) Gives the readily detonated lead dinitrotolyloxide. (e)  $208-215^{\circ}$ .  $\gamma$ -Trinitrotoluene [3:4:6] (a) m. p.  $104^{\circ}$ . (b) Granulates. (c) and (d) As with  $\beta$ -compound. (e)  $193-198^{\circ}$ .  $\delta$ -Trinitrotoluene [3:4:5] (a) m. p.  $137.5$  ( $134^{\circ}$ ). (b), (c), and (d) As with  $\gamma$ -compound. (e)  $252^{\circ}$ .  $\epsilon$ -Trinitrotoluene [2:3:6] (a) m. p.  $111^{\circ}$ . (b) Needles. (c) Some sodium dinitrotolyloxide very slowly formed. (d) Almost unattacked. (e)  $249-250^{\circ}$ .  $\zeta$ -Trinitrotoluene [2:3:5] (a)  $97^{\circ}$ . (b) Granulates. (c) and (d) As with  $\beta$ -compound. (e)  $268-271^{\circ}$ . T. S. W.

#### Solubility of 2:4:6-Trinitrotoluene in Organic Solvents.

J. A. TAYLOR and WM. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1923, 45, 44-59).—The solubility of 2:4:6-trinitrotoluene has been determined at a series of temperatures in water, aniline, pyridine, toluene, acetone, benzene, carbon tetrachloride, 95% ethyl alcohol, chloroform, carbon disulphide, and diethyl ether. An equimolecular compound is formed in pyridine solution which exists at temperatures below  $40^{\circ}$  and melts at  $40-42^{\circ}$ . The following data are recorded, in grams per 100 g. of solvent: water,  $3^{\circ}$ , 0.0110;  $5.9^{\circ}$ , 0.0113;  $20.0^{\circ}$ , 0.0120;  $33.1^{\circ}$ , 0.0203;  $44.2^{\circ}$ , 0.0340;  $45^{\circ}$ , 0.0370;  $53.0^{\circ}$ , 0.0534;  $57.15^{\circ}$ , 0.0614;  $73.25^{\circ}$ , 0.0963;  $84.4^{\circ}$ , 0.1375, and  $99.5^{\circ}$ , 0.1467; ether,  $0.3^{\circ}$ , 1.75;  $5.9^{\circ}$ , 2.13;  $20.3^{\circ}$ , 3.33;  $26.0^{\circ}$ , 3.92, and  $33.0^{\circ}$ , 5.15; 95% alcohol,  $0.3^{\circ}$ , 0.70;  $32.0^{\circ}$ , 1.99;  $40.1^{\circ}$ , 2.98;  $45.0^{\circ}$ , 3.70;  $50.0^{\circ}$ , 4.61;  $55.0^{\circ}$ , 6.08;  $59.8^{\circ}$ , 8.14;  $65.0^{\circ}$ , 11.40, and  $74.0^{\circ}$ , 18.58; carbon disulphide,  $0.3^{\circ}$ , 0.158;  $5.6^{\circ}$ , 0.20;  $11.1^{\circ}$ , 0.27;  $24.5^{\circ}$ , 0.62;  $30.1^{\circ}$ , 0.84;  $35.0^{\circ}$ , 1.12;  $40.0^{\circ}$ , 1.53;  $45.0^{\circ}$ , 2.02, and  $46.3^{\circ}$ , 2.20; carbon tetrachloride,  $0.3^{\circ}$ , 0.22;  $5.6^{\circ}$ , 0.28;  $11.1^{\circ}$ , 0.37;  $24.5^{\circ}$ , 0.76;  $35.0^{\circ}$ , 1.32;  $45.0^{\circ}$ , 2.37;  $57.0^{\circ}$ , 5.33;  $61.7^{\circ}$ , 8.14;  $67.0^{\circ}$ , 13.68;  $72.5^{\circ}$ , 20.72, and  $78.2^{\circ}$ , 29.76; chloroform,  $0.3^{\circ}$ , 6.33;  $32.0^{\circ}$ , 37.7;  $40.1^{\circ}$ , 66.6;  $50.0^{\circ}$ , 101;  $50.0^{\circ}$ , 150;  $55^{\circ}$ , 218;  $59.8^{\circ}$ , 296, and  $65.0^{\circ}$ , 442. The other solvents mentioned above dissolve very large quantities of trinitrotoluene, and in these cases the solubility was determined by the cooling-curve method. The whole of the values are recalculated to grams per 100 g. of solvent and tabulated, giving the solubility for temperatures in  $5^{\circ}$  intervals over the whole range examined.

J. F. S.

**Preparation of Salts of 1 : 3-Dinitro-4 : 5-dinitrosobenzene.** HANS RATHSBURG (Brit. Pat. 190844).—Sparingly soluble salts of 1 : 3-dinitro-4 : 5-dinitrosobenzene are obtained by heating picryl chloride (25 kg.) in aqueous suspension with a solution of sodium azide (7 kg.) in 300 litres of water for one hour at 80–90°, and for three hours at 90–100°, whereby the picryl azide first formed is transformed with loss of nitrogen into 1 : 3-dinitro-4 : 5-dinitrosobenzene, which is separated from the mother-liquors, converted into its sodium salt by treatment with sodium hydroxide, and then in the moist state is allowed to react with the acetate or chloride of the metal of which the dinitrodinitrosobenzene salt is required.

G. F. M.

**Sulphinic Acids.** JULIUS VON BRAUN and WILHELM KAISER (Ber., 1923, 56, [B], 549–553).—The action of aromatic sulphonyl chlorides on dithiocarbamates takes place unexpectedly in accordance with the scheme  $2\text{NR}_2 \cdot \text{CS} \cdot \text{SH} \cdot \text{NHR}_2 + \text{Cl} \cdot \text{SO}_2 \cdot \text{R}^1 = \text{NR}_2 \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{NR}_2 + \text{NHR}_2 \cdot \text{HCl} + \text{SO}_2 \cdot \text{H} \cdot \text{R}^1 \cdot \text{NHR}_2$ , and thus affords a ready method of preparing sulphinic acids. The conversion of the latter into amides has not been effected previously (Knoevenagel and Polak, A., 1908, i, 971; Hilditch and Smith, A., 1909, i, 18). It is now shown that the transformation occurs normally in the presence of an indifferent solvent, but that the new amides are much more readily decomposed than the analogous carboxylamides; they are unable to yield derivatives of the amide-chloride and imide-chloride types.

Dimethylamine, carbon disulphide, and benzenesulphonyl chloride give tetramethylthiuram disulphide, m. p. 150–154°, (?) benzenesulphondimethylamide, and benzenesulphinic acid, m. p. 83°, which is conveniently isolated through its ferric salt (cf. Thomas, T., 1909, 95, 342). Piperidine, carbon disulphide, and benzenesulphonyl chloride give dipiperidylthiuram disulphide, m. p. 128°, and benzenesulphinic acid. *p*-Toluenesulphinic acid, m. p. 84°, is prepared from piperidine, carbon disulphide, and *p*-toluenesulphonyl chloride, whilst tetrahydronaphthalene- $\beta$ -sulphonyl chloride gives dipiperidylthiuram disulphide, tetrahydronaphthalene- $\beta$ -sulphonylpiperidine,  $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_{10}$ , m. p. 98–100°, and tetrahydronaphthalene- $\beta$ -sulphinic acid, colourless needles, m. p. 87–88°.

Benzenesulphinanilide,  $\text{SOPh} \cdot \text{NHPh}$ , m. p. 112–114°, is prepared by the action of benzenesulphonyl chloride on two molecular proportions of aniline dissolved in ether at 0°. It is extensively decomposed by boiling acids without appearing to undergo a smooth fission into benzenesulphinic acid and aniline, which can, however, be brought about by cold, aqueous-alcoholic alkali hydroxide solutions. Benzenesulphinpiperidine has m. p. 83° after softening at 80°; it is energetically attacked by phosphorus pentachloride even in the presence of chloroform, and gives chlorinated compounds, the reaction appearing to occur in a direction different from that of benzoylpiperidine. Benzenesulphindimethylamide,  $\text{SOPh} \cdot \text{NMe}_2$ , is a yellow liquid, b. p. 90°/2–3 mm. Benzenesulphinamide has m. p. 121°. Toluene-*p*-sulphonyl chloride, b. p.

115—120°/4 mm., is converted in a similar manner into the corresponding *anilide*, m. p. 138°, and *amide*, colourless needles, m. p. 120° after softening at 117°.

H. W.

**Alkylamides of Aromatic Sulphonic Acids.** W. BADER and D. A. NIGHTENGALE (U.S. Pat. 1433925).—When xylenesulphonyl chloride and methylamine hydrochloride are heated with sodium carbonate at 80—100° in presence of moisture not exceeding 5%, xylenesulphonmethylamide is produced and may be recovered by extraction with benzene. The instance quoted is an example of a reaction of more general application. Benzene or other diluents may be present.

CHEMICAL ABSTRACTS.

**Preparation of Aromatic Sulphones.** G. FOUQUE and J. LACROIX (*Bull. Soc. chim.*, 1923, [iv], 33, 180—183).—By the prolonged action of sulphuric acid on aromatic hydrocarbons or their derivatives under such conditions that the water formed during the reaction and condensing in the reflux condenser is not allowed to run back into the reaction mixture, aromatic sulphones were obtained in good yield. Their formation may be due to the action of a further quantity of hydrocarbon on the sulphonic acid produced, as, for example, with benzene,  $\text{PhSO}_3\text{H} + \text{C}_6\text{H}_6 = \text{SO}_2\text{Ph}_2 + \text{H}_2\text{O}$ , or more probably by reason of the decomposition of the sulphonic acid under the influence of heat and in the absence of water, thus:  $2\text{PhSO}_3\text{H} = \text{SO}_2\text{Ph}_2 + \text{H}_2\text{SO}_4$ . The conditions required for the reaction were obtained by interposing between the reflux condenser and the reaction vessel a flask with a side tubulure in the bulb, a tube bent at right angles passing through this tubulure and connecting with the neck of the reaction flask. By this means the water and the hydrocarbon condensing in the reflux condenser flow back into the tubulated flask and separate into two layers, and consequently only the lighter hydrocarbon flows back through the tubulure into the reaction flask. When the substance to be sulphonated is heavier than water, the connecting tube is bent downwards to the bottom of the tubulated flask, so that the lower layer passes back into the reaction flask instead of the upper aqueous layer; a small orifice on the upper side of the tube just before the bend serves for the passage of the vapours from the reaction flask. By means of this apparatus diphenylsulphone, m. p. 128°, *di-p-chlorodiphenylsulphone*, m. p. 146°, *di-p-bromodiphenylsulphone*, m. p. 171°, and *di-p-hydroxydiphenylsulphone*, m. p. 240°, were prepared.

G. F. M.

**Doubly Refractive Naphthalene.** W. KIRBY (*J. Soc. Chem. Ind.*, 1923, 42, 58T).—When naphthalene, m. p. 80·7°,  $d_4^{20}$  1·185, is melted in a suitable vessel and allowed to cool, the substance in contact with the sides of the vessel solidifies to form a clear, transparent mass which is doubly refractive; the resolving power is more than 30% greater than that of Iceland spar.

W. P. S.

**Some Fluoro-derivatives of Diphenyl.** THÉO VAN HOVE (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 505—530; *Bull. Soc. chim. Belg.*, 1923, 32, 52—70).—Diphenyl (500 g.) is nitrated in the cold

with an acetic acid solution containing 2 mols. of nitric acid (*d* 1.5). After a time, most of the 4-nitrodiphenyl separates, and from the mother-liquor, by precipitation with water, etc., and distillation under diminished pressure, 2-nitrodiphenyl (195 g.) is obtained, b. p. 200—205°/30 mm., together with more 4-nitrodiphenyl (350 g. in all).

In the reduction of 4-nitrodiphenyl by means of tin and hydrochloric acid, the sparingly soluble chlorostannate is best separated by filtration. 4-Aminodiphenyl boils at 210—212°/25 mm. 2-Aminodiphenyl forms a soluble chlorostannate, and boils at 189—191°/30 mm.

4-Fluorodiphenyl, obtained by diazotising 4-aminodiphenyl in hydrofluoric acid solution, and subsequently heating at 60°, forms colourless plates, m. p. 74.2°, b. p. 253°, and is volatile in steam. 2-Fluorodiphenyl, obtained similarly, colourless prisms, m. p. 73.5°, b. p. 248°, is also volatile in steam.

The nitration of 4-fluorodiphenyl in acetic acid solution, using nitric acid (*d* 1.5), gave three products: (a) 4-fluoro-4'-nitrodiphenyl, needles, m. p. 123°, giving *p*-nitrobenzoic acid on oxidation; (b) an approximately equal weight of 4-fluoro-2'-nitrodiphenyl, needles, m. p. 59—60°, giving, on oxidation, *p*-fluorobenzoic acid, and (c) a very small quantity of 4-fluoro-2-nitrodiphenyl, prisms, m. p. 53—54°, giving, on oxidation, 4-fluoro-2-nitrobenzoic acid, m. p. 130°. In the first experiment, but never subsequently, the author obtained pale yellow prisms, m. p. 43—43.5°, which, on keeping, became opaque, and then melted at 58°. This is apparently a case of dimorphism.

4-Fluoro-4'-aminodiphenyl, obtained by the reduction of the corresponding nitro-compound, forms colourless leaflets, m. p. 120°; hydrochloride, sparingly soluble leaflets; sulphate and oxalate, very sparingly soluble leaflets; acetyl derivative, m. p. 205—205.5°.

4-Fluoro-2'-aminodiphenyl, colourless crystals, m. p. 42—42.5°, b. p. 186—187°/40 mm., forms a hydrochloride, m. p. about 210°, and a sulphate, which are much more soluble than the corresponding salts of the 4'-derivative. The amine, on oxidation, gives *p*-fluorobenzoic acid and yields an acetyl derivative, m. p. 120°.

4-Fluoro-2-nitrodiphenyl, on reduction, gives an amine, the acetyl derivative of which melts at 98°.

2-Fluorodiphenyl gives rise to three isomeric nitro-derivatives: (a) a small quantity of colourless needles, m. p. 81°, probably 2-fluoro-4-nitrodiphenyl, since the acetyl derivative (colourless prisms, m. p. 155°) of the amine obtained by reduction gives, on oxidation, benzoic acid, (b) 2-fluoro-4'-nitrodiphenyl, yellow needles, m. p. 74.5°, giving, on oxidation, *p*-nitrobenzoic acid, and (c) 2-fluoro-2'-nitrodiphenyl, prisms, m. p. 71.5°, giving *o*-nitrobenzoic acid on oxidation.

2-Fluoro-2'-aminodiphenyl, colourless crystals, m. p. 91°, gives a very soluble hydrochloride, m. p. about 205°, a soluble sulphate, and an acetyl derivative, colourless needles, m. p. 102°. 2-Fluoro-4'-aminodiphenyl, m. p. 36°, b. p. 199—201°/25 mm., gives a sparingly soluble hydrochloride, m. p. above 250°, a sparingly soluble sulphate, and an acetyl derivative, m. p. 147—148°.

In the nitration of diphenyl, small quantities of a yellow, crystalline solid, m. p.  $202^{\circ}$ , probably 3 : 5 : 4'-trinitro-4-hydroxydiphenyl, are formed. 4-Fluorodiphenyl, similarly, gives rise to a small quantity of a solid,  $C_{12}H_7O_3N_3F$  (?), probably a fluorodinitro-hydroxydiphenyl.

E. E. T.

**The Products of the Bromination of *as*-Diphenylethylene.**  
P. LIPP (*Ber.*, 1923, 56, [B], 567—571).—The author's experiences in the bromination of camphene has led him to examine the behaviour of other asymmetrically substituted ethylenes, and for this purpose *as*-diphenylethylene,  $CPh_2:CH_2$ , has been selected. Under certain conditions, the normal dibromide can be isolated, but it passes somewhat readily into diphenylvinyl bromide. Under drastic treatment, the latter substance suffers rearrangement of the diphenylvinyl residue, whereas under milder conditions the radicle remains intact.

[In part with W. LÜDICKE].— $\alpha\beta$ -Dibromo- $\alpha\alpha$ -diphenylethane,  $CPh_2Br:CH_2Br$ , is obtained by the gradual addition of a solution of dry bromine in carbon disulphide to *as*-diphenylethylene dissolved in the same medium at a temperature not exceeding  $0^{\circ}$  and subsequent removal of the solvent in a vacuum at the atmospheric temperature; it crystallises in coarse plates or prisms, decomp.  $63$ — $64^{\circ}$  (corr.). When pure, it may be preserved unchanged for weeks, but rapidly passes when heated into diphenylvinyl bromide, m. p.  $41$ — $42^{\circ}$ . It is converted by methyl-alcoholic potassium hydroxide solution into  $\beta$ -bromo- $\alpha$ -methoxy- $\alpha\alpha$ -diphenylethane,  $OMe:CPh_2:CH_2Br$ , short prisms or plates, m. p.  $73$ — $74.5^{\circ}$  (corr.), which is unaffected by boiling dimethylaniline or aqueous potassium hydroxide solution; molten potassium hydroxide converts it into toluene,  $CPh:CPh$ .  $\beta$ -Bromo- $\alpha$ -ethoxy- $\alpha\alpha$ -diphenylethane crystallises in long prisms, m. p.  $98$ — $99^{\circ}$  (corr.).

Diphenylvinyl bromide is transformed by molten potassium hydroxide into toluene, b. p.  $158$ — $160^{\circ}/10.5$  mm., m. p.  $60^{\circ}$  (corr.) [dibromide, m. p.  $211^{\circ}$  (corr.)]. It reacts with activated magnesium in the presence of ether, and the product after treatment with carbon dioxide yields  $\beta\beta$ -diphenylacrylic acid,  $CPh_2:CH:CO_2H$ , m. p.  $162^{\circ}$  (the sodium salt is relatively sparingly soluble in water), and  $\alpha\alpha\beta\beta$ -tetraphenyl- $\Delta^4$ -butadiene, colourless, thin prisms, m. p.  $205$ — $206^{\circ}$  (corr.).

H. W.

**Crystalline Form of 4-Chloro-2-bromo-3-nitroacetanilide.**  
MARIA DE ANGELIS (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 450—453, 524—529; cf. A., 1920, i, 608, 834).—This compound is dimorphous. The metastable  $\alpha$ -modification,  $d$  1.857, forms crystals belonging to the prismatic class of the monoclinic system,  $a:b:c=1.2985:1:0.5728$ ,  $\beta=86^{\circ}43'$ . The stable  $\beta$ -modification,  $d$  1.891, was not obtained in crystals capable of being measured accurately, but appears to be isomorphous with 2:4-dibromo-3-nitroacetanilide (A., 1920, i, 834).

A mixture of 4-chloro-2-bromo-3-nitroacetanilide (1 mol.) with the dibromo-analogue (1 mol.) yields triclinic crystals isomorphous with those of the dibromo-compound (*loc. cit.*, 834). A similar

mixture of 4-chloro-2-bromo-3-nitroacetanilide with the dichloro-compound yields tabular, monoclinic crystals isomorphous with the  $\beta$ -form of the dichloro-derivative (*loc. cit.*, 608), or, less readily, metastable, prismatic crystals of the monoclinic system, isomorphous with those of the metastable modification of 4-chloro-2-bromo-3-nitroacetanilide. T. H. P.

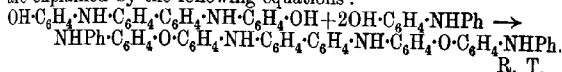
**Solubility of Trinitrophenylmethylnitroamine (Tetryl) in Organic Solvents.** C. Å. TAYLOR and WM. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1923, 45, 104—107).—The solubility of tetryl has been determined in water, ether, 95% alcohol, carbon disulphide, chloroform, and carbon tetrachloride at a large number of temperatures. The following solubilities in grams of tetryl per hundred grams of solvent are recorded: Water, 0.5°, 0.0051; 9.6°, 0.0069; 14.8°, 0.0071; 20.5°, 0.0074; 30°, 0.0084; 35°, 0.0094; 40°, 0.0107; 45°, 0.0135; 50.0°, 0.0200; 60.05°, 0.0350; 65.05°, 0.0443; 69.5°, 0.0531; 84.2°, 0.0952; 96.7°, 0.1619, and 98.55°, 0.1755; ether, 0.4°, 0.1918; 9.6°, 0.3174; 20.5°, 0.4219; 29.05°, 0.4680, and 30.0°, 0.4713; 95% alcohol, 0.5°, 0.324; 25.0°, 0.648; 33.0°, 0.843; 39.0°, 1.08; 45.1°, 1.39; 51.0°, 1.81; 61.0°, 2.76; 70.05°, 4.23, and 77.1°, 5.80; carbon disulphide, 0.4°, 0.0094; 15.0°, 0.0177; 28.0°, 0.0277; 37°, 0.0437; 40°, 0.0557, and 46.1°, 0.1048; chloroform, 0.4°, 0.282; 15°, 0.473; 28.0°, 0.740; 32.2°, 0.856; 40.0°, 1.209; 50.0°, 1.780, and 58.8°, 2.53; carbon tetrachloride, 0.4°, 0.0073; 25.0°, 0.0304; 33.0°, 0.0449; 39.0°, 0.0566; 45.1°, 0.0733; 51.0°, 0.0997; 61.0°, 0.1597; 70.05°, 0.2419, and 73.25°, 0.2773. A table is drawn up giving the interpolated values for every 5° for each solvent over the range investigated. J. F. S.

**Chloroacetyl-*p*-anisidine and its Nitro-derivatives.** FRÉ. DÉRIC REVERDIN (*Helv. Chim. Acta*, 1923, 6, 87—93).—Chloroacetyl-*p*-anisidine is much more resistant to hydrolysis by acids than the corresponding acetyl, benzoyl, and toluenesulphonyl compounds. It has also to be nitrated under conditions unlike those which give the best results in the case of other acyl-derivatives of *p*-anisidine. The mono-nitro-derivative was obtained by dissolving the chloroacetyl-*p*-anisidine (12 g.) in glacial acetic acid (120 c.c.) and running in the nitric acid gradually at 10° (15 c.c., *d* 1.52). The principal product, 3-nitrochloroacetyl-*p*-anisidine, yield 80—82% of theory, forms yellow needles, *m. p.* 104°. A small amount of 2-nitrochloroacetyl-*p*-anisidine, yellow needles, *m. p.* 153°, was also obtained. Like the parent substance, the nitro-derivatives are unusually resistant to acid hydrolysis, but are rapidly hydrolysed to nitroanisidine by 4% potassium hydroxide solution. 2:3-Dinitrochloroacetyl-*p*-anisidine was obtained by nitrating 3-nitrochloroacetyl-*p*-anisidine with nitric acid, *d* 1.52, at the ordinary temperature, finishing at 45°; it forms white, prismatic needles, *m. p.* 172°. A small amount of 2:5-dinitrochloroacetyl-*p*-anisidine was formed at the same time, yellow needles, *m. p.* 128°. 2:3:5-Trinitrochloroacetyl-*p*-anisidine could only be obtained by nitrating the dinitro-compound with mixed

nitric and concentrated sulphuric acids, and the best yield obtained was only 40% of theory. It forms white needles, m. p. 245—246°. The nitro-compounds do not appear to form additive compounds with bases. With aniline, however, 3-nitrochloroacetyl-*p*-anisidine forms a compound which appears to be 3-nitroanilino-acetyl-*p*-anisidine,  $\text{OMe}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHPh}$ , yellow spangles, m. p. 143°. 2:3-Dinitrochloroacetyl-*p*-anisidine forms with aniline a compound, orange needles, m. p. 153°, containing no chlorine; the trinitro-derivative gives a similar compound, m. p. 172—173°.

E. H. R.

**The Products of the Oxidation of Diphenylamine with Hydrogen Peroxide.** P. P. ROUBCOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 137—139).—Uschakov (A., 1906, i, 159; 1907, i, 361) isolated two substances,  $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_2$ , and  $\text{C}_{60}\text{H}_{40}\text{O}_2\text{N}_2$ , from the products of the oxidation of diphenylamine with hydrogen peroxide. The first of these he showed to have the structure  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , and to be formed by the condensation of two molecules of hydroxydiphenylamine. The structure of the second was not determined. It is now suggested that its empirical formula should be  $\text{C}_{48}\text{H}_{36}\text{O}_2\text{N}_4$ , and that the presence of traces of diphenylamine (about 0.15%) could have caused the discrepancy in analysis. Its formation and structure are explained by the following equations:



R. T.

**Action of the Oxides and the Oxy-acids of Nitrogen on Diphenylurethane.** HUGH RYAN and ANNE DONNELLAN (*Proc. Roy. Dublin Soc.*, 1923, 17, 113—118).—It has already been shown (A., 1919, i, 481, 482) that diphenylnitrosoamine can be nitrated more readily than diphenylamine; this is ascribed to the protective influence of the nitroso-group. The nitration of diphenylurethane has now been systematically investigated (cf. Hager, A., 1886, 59).

Nitric acid at the ordinary temperature and at low concentrations in acetic acid solution has apparently no action; under similar conditions in carbon tetrachloride solution, 4:4'-dinitrodiphenylurethane, 2:4'-dinitrodiphenylurethane (cf. Hager, *loc. cit.*), and 4-nitrodiphenylurethane, colourless prisms, m. p. 68°, are formed. Cold concentrated nitric acid (*d* 1.42) converts the urethane into its 4-nitro-derivative, whilst cold fuming nitric acid gives the 4:4'- and the 2:4'-dinitro-derivatives. Diphenylurethane, or its 4-nitro-derivative, is converted by a mixture of concentrated nitric and sulphuric acids into 2:4:2':4'-tetranitrodiphenylurethane, yellowish-white, flat prisms, m. p. 184—185°, which reacts further with the hot mixed nitrating acids to give 2:4:6:2':4':6'-hexanitrodiphenylamine. Diphenylurethane reacts in carbon tetrachloride solution with nitrogen peroxide, giving the 4:4'- and the 2:4'-dinitro-derivatives.

Notwithstanding the similarity in structure between diphenyl-

urethane and diphenylnitrosoamine, the former is less readily nitrated than the latter, the nitration at low temperatures and concentrations stopping at the dinitro-stage.

Attempts to synthesise the nitrodiphenylurethanes from ethyl chloroformate and the relevant nitrodiphenylamines were unsuccessful; their constitutions have, however, been proved by hydrolysis to the corresponding nitro-derivatives of diphenylamine.

W. S. N.

**Action of the Oxides and the Oxy-acids of Nitrogen on Ethyl-*o*-tolylurethane.** HUGH RYAN and NICHOLAS CULLINANE (*Proc. Roy. Dublin Soc.*, 1923, 17, 119—124; cf. preceding abstract).—Ethyl-*o*-tolylurethane, a colourless oil, b. p. 225°, is less readily nitrated than diphenylamine; moreover, the ethyl group is slowly eliminated, and the nitro-products are in all cases derived from *o*-tolylurethane.

Nitrogen peroxide (vapour) converts the urethane into oxalic acid and 5-nitro-*o*-tolylurethane, m. p. 137° (Vittenet, A., 1899, i, 756, gives 127°), identical with the product formed by the action of ethyl chloroformate on 5-nitro-*o*-toluidine. In carbon tetrachloride solution, fuming nitric acid converts ethyl-*o*-tolylurethane into 3:5-dinitro-*o*-tolylurethane, slender, white needles, m. p. 159—160°, which could not be further nitrated, and is also produced by the nitration of 5-nitro- or 3-nitro-*o*-tolylurethane; the synthesis of the latter, almost colourless prisms, m. p. 131°, and of 4-nitro-*o*-tolylurethane, by the action of ethyl chloroformate on 3-nitro-*o*-toluidine or 4-nitro-*o*-toluidine, respectively, are described.

4-Nitro-*o*-tolylurethane, m. p. 137° (Vittenet, *loc. cit.*, gives 129°), is converted by heating with fuming nitric acid into slender, white needles, m. p. 193—194° (decomp.), probably 4:5-dinitro-*o*-tolylurethane.

W. S. N.

**Action of the Oxides and the Oxy-acids of Nitrogen on Phenylethylurethane.** HUGH RYAN and ANNA CONNOLLY (*Proc. Roy. Dublin Soc.*, 1923, 17, 125—130; cf. preceding abstracts).—Like other urethanes, phenylethylurethane nitrates with difficulty. Unlike *o*-tolylethylurethane, it yields nitro-derivatives of the tertiary urethane when nitrated at a low temperature, although at moderately high temperatures derivatives of phenylurethane are produced.

Nitrogen peroxide in carbon tetrachloride solution converts the urethane into 4-nitrophenylethylurethane, large, colourless rhombohedra, m. p. 55—56°, and into a dinitro-compound, colourless, rhombic prisms, m. p. 88—89°, probably 2:4-dinitrophenylethylurethane; the former is converted by boiling with alcoholic potash into *p*-nitroethylaniline, but the conversion of the dinitro-compound into 2:4-dinitroethylaniline has not yet been accomplished.

The same two nitro-derivatives are obtained by the action of cold fuming nitric acid on phenylethylurethane, but when the temperature is allowed to rise during the reaction, the chief products are 4-nitrophenylurethane and 2:4-dinitrophenylurethane. A mixture of concentrated nitric and sulphuric acids converts

phenylethylurethane into 2:4-dinitro- and 2:4:6-trinitro-phenylurethanes.

At low concentrations in acetic acid solution and at the ordinary temperature, the urethane is converted very slowly and incompletely by nitric acid into its mononitro- and dinitro-derivatives; but in carbon tetrachloride solution the substances react more readily, with formation of 4-nitrophenylethylurethane.

W. S. N.

**Action of the Oxides and the Oxy-acids of Nitrogen on Phenylbenzylurethane.** HUGH RYAN and JAMES L. O'DONOVAN (*Proc. Roy. Dublin Soc.*, 1923, 17, 131—137; cf. preceding abstracts).

—Like other tertiary aromatic urethanes, *phenylbenzylurethane*, a colourless oil, is difficult to nitrate. The benzyl radicle can, however, be nitrated, as well as the phenyl radicle, without decomposition of the urethane.

Nitrogen peroxide converts the urethane into *p*-nitrophenylbenzylurethane, almost colourless plates, m. p. 70—71°, and a trinitro-(2:4:4'- or 2:2':4'-)-phenylbenzylurethane, long, rhombic crystals, m. p. 110—111°; a little oxalic acid is also formed. The use of cold dilute nitric acid leads to the above mononitro-compound and oxalic acid; at higher concentrations of the acid, the trinitro-derivative is produced. Warm concentrated nitric acid converts the urethane into a tetranitro-derivative, colourless plates, m. p. 126—127°, probably 2:4:2':4'-tetranitrophenylbenzylurethane, and a compound, yellowish-white, silky needles, m. p. 274° (decomp.), probably 2:4:6:2':4'-pentanitrophenylbenzylamine. Secondary reactions also occur leading to *p*-nitrobenzoic acid, 2:4-dinitrophenylurethane, and a compound, yellow, felted needles, m. p. 264° (decomp.), either pentanitrophenylbenzylurethane or trinitrophenylbenzylamine.

The mononitro-derivative (above) is converted on being boiled with alcoholic potash into *p*-nitrophenylbenzylamine; its constitution is thereby established. It is, moreover, different from phenyl-*p*-nitrobenzylurethane, rhombic plates, m. p. 68—69°, which is formed by the condensation of ethyl chloroformate with phenyl-*p*-nitrobenzylamine.

W. S. N.

**Preparation of Arylthiocarbimides.** F. B. DAINS, R. Q. BEWSTER, and C. P. OLANDER (*Univ. Kansas Sci. Bull.*, 1922, 13, 1—14; cf. Hofmann, *Ber.*, 1882, 15, 986; Werner, *T.*, 1891, 59, 400; Dains, *A.*, 1900, i, 390; Anschütz, *A.*, 1910, i, 158; Braun, *A.*, 1904, i, 90; Losanitsch, *A.*, 1892, 55; Heller and Bauer, *A.*, 1902, i, 444).—The authors find that Losanitsch's method (*loc. cit.*) is generally applicable to the preparation of aryl thiocarbimides. As a modification of Heller and Bauer's method (*loc. cit.*), 54 g. of aniline are added with cooling and constant stirring during fifteen minutes to 54 g. of carbon disulphide and 80 g. of 28% ammonia solution. Ammonium phenyldithiocarbamate separates, and after being kept in ice for an hour is collected, washed with ethyl alcohol, and dried on a plate. On keeping, hydrogen sulphide, ammonia, carbon disulphide, aniline,

and thiocarbanilide are formed, the decomposition being hastened when the salt is boiled with water. Ammonium *p*-chloro- and *p*-bromo-phenyldithiocarbamate give 55–60% yields of the substituted thiocarbanilide. With hydrochloric acid, ammonium phenyldithiocarbamate reacts quantitatively according to the equation:  $\text{NHPh-CS-SNH}_4 + 2\text{HCl} = \text{NH}_2\text{Ph.HCl} + \text{CS}_2 + \text{NH}_4\text{Cl}$ . For the production of arylthiocarbimides from ammonium aryl-dithiocarbamates, a salt must be used which will give a stable sulphide and an ammonium salt. Ferrous sulphate, zinc sulphate, copper sulphate, and lead nitrate with ammonium phenyldithiocarbamate, after keeping and distillation with steam, give, respectively, a yield of 3 c.c., 23%, 71.7%, and 77.2% of phenylthiocarbimide. Phenylthiocarbimide is prepared as follows. Ammonium phenyldithiocarbamate is obtained (see above), the mixture being stirred for thirty minutes after addition of the aniline, and then kept for thirty minutes without stirring. The precipitate is dissolved in 80 c.c. of water, 200 g. of lead nitrate in 400 c.c. of water are added with stirring, and the mixture is distilled with steam from a 5-litre flask; the receiver should contain dilute sulphuric acid to prevent formation of thiocarbanilide. Replacement of the ammonium by the sodium salt results in a yield of only 30.2% of phenylthiocarbimide. The barium salt and zinc chloride gave a 37.4% yield, and in the case of the calcium salt very little phenylthiocarbimide is formed, the main product being thiocarbanilide. The following thiocarbimides were prepared: *o*-tolyl- (yield 73.27%), *m*-tolyl-, *p*-tolyl-, *m*-4-xylyl-, *m*. *p*. 31°; *ψ*-cumyl-,  $\alpha$ - and  $\beta$ -naphthyl-, *o*- and *p*-anisyl-, and *p*-phenetidyl-; *m*- and *p*-bromophenyl-, *p*-chlorophenyl-, and *p*-iodophenyl-derivatives were also formed, but ammonium *p*-nitrophenyldithiocarbamate could not be prepared. The success of the method is dependent on the completeness of the formation of the ammonium arylthiocarbamate, on the ease and completeness of separation from the sulphide precipitate, and on the avoidance of side reactions.

CHEMICAL ABSTRACTS.

**Pinacolin Transformations. V. The Transformation of Compounds containing Six- and Seven-membered Carbon Rings.** HANS MEERWEIN and JOSEPH SCHÄFER (*J. pr. Chem.*, 1922, [iii], 104, 289–310; cf. *A.*, 1910, i, 856; 1913, i, 485; 1914, i, 850; 1919, i, 162).—The authors have shown that both 1:1-dimethylcycloheptan-2-ol and 1-methyl-1- $\alpha$ -hydroxyethylcyclohexane give on dehydration a mixture of 1:2-dimethyl- $\Delta^1$ -cycloheptene and  $\Delta^1$ -isopropylcyclohexene, in a proportion which cannot exactly be estimated.

The behaviour of 1:1-dimethylcycloheptan-2-ol is therefore comparable with that of 1:1-dimethylcyclohexan-2-ol, which similarly gives 1:2-dimethyl- $\Delta^1$ -cyclohexene (75%) and  $\Delta^1$ -isopropylcyclopentane; hence, from this comparison, no difference in the stability of six-membered and seven-membered rings can be detected. Nevertheless, whilst the dehydration of 1-methyl-1- $\alpha$ -hydroxyethylcyclopentane gives exclusively 1:2-dimethyl-

$\Delta^1$ -cyclohexene, with formation of a larger ring, the analogous production from 1-methyl-1- $\alpha$ -hydroxyethylcyclohexane of 1:1-dimethyl- $\Delta^1$ -cycloheptene is accompanied by the formation of  $\Delta^1$ -isopropylcyclohexene, by the wandering of a methyl group; moreover, whilst  $\alpha$ -cyclohexyl- $\beta$ -methylpropan- $\alpha\beta$ -diol on dehydration gives 1:1-dimethylcyclohexan-2-one only,  $\alpha$ -cyclohexyl- $\beta$ -methylpropan- $\alpha\beta$ -diol gives, besides 1:1-dimethylcycloheptan-2-one, some 1-acetyl-1-methylcyclohexane. Hence in both cases there is an undoubted resistance to seven-ring formation.

Nevertheless, the ready conversion of six- into seven-membered rings calls for comment, since it is improbable according to Baeyer's strain theory. The authors consider that polymethylene rings assume, as far as possible, strain-free configurations (cf. A., 1922, i, 441; this vol., i, 224; also Baker and Ingold, T., 1923, 123, 122); hence six-membered and larger rings lie in more than one plane. This view appears at first sight to conflict with the difficulty experienced in closing seven-membered and larger rings. The formation of a ring from an open chain must, however, proceed from a configuration of the latter corresponding with the strain-free configuration of the ring (cf. A., 1919, ii, 229). The more complicated the latter, the less frequently will this favourable configuration of the chain occur; hence the small tendency to production of large rings from open-chain substances is explicable without reference to strains (cf. Wojnicz-Sianozencki, A., 1922, i, 330). On the other hand, it is remarked, the strain-free configurations of cyclohexane and cycloheptane being very similar, interconversion of their derivatives requires but little intramolecular rearrangement, and the ease of the change is therefore not surprising.

When the product of the action of sulphuric acid on  $\alpha$ -cyclohexyl- $\beta$ -methylpropan- $\alpha\beta$ -diol (A., 1913, i, 485; cf. Tarboureich, A., 1913, i, 181) is oxidised by means of excess of sodium hypobromite, the 1-methyl-1-acetylcyclohexane is converted into 1-methylcyclohexane-1-carboxylic acid, which can then be separated from the 1:1-dimethylcycloheptan-2-one, b. p.  $190^\circ$ ,  $d_4^{20}$  0.9205,  $n_D^{20}$  1.45694, semicarbazone, long, colourless needles, m. p.  $169-170^\circ$  (Tarboureich, 176°), oxime, tabular crystals, m. p.  $83-85^\circ$ . Reduction of this ketone by means of sodium in moist ethereal solution gives 1:1-dimethylcycloheptan-2-ol, b. p.  $86.8-87.2^\circ/13$  mm.,  $d_4^{20}$  0.9345,  $n_D^{20}$  1.47478, which gives a phenylurethane, long needles, m. p.  $100-101^\circ$ , and is converted in 80% yield, by heating at  $180^\circ$  with zinc chloride, into a mixture of hydrocarbons, b. p.  $155.1-156.3^\circ$ ,  $d_4^{20}$  0.8274,  $n_D^{20}$  1.46073, from which the nitrosochloride of  $\Delta^1$ -isopropylcyclohexene (cf. Wallach, A., 1908, i, 402) and a second nitrosochloride, m. p. about  $118^\circ$ , blue crystals which become colourless (probably that of 1:2-dimethyl- $\Delta^1$ -cycloheptene), have been isolated. Oxidation of the hydrocarbon mixture in glacial acetic acid solution by means of ozone leads to known products, (a)  $\beta\gamma$ -diketononane (Blaise and Köhler, A., 1909, i, 204) derived from 1:2-dimethyl- $\Delta^1$ -cycloheptene, which is therefore present in the mixture; (b) the acid  $\text{CO}_2\text{H}[\text{CH}_2]_4\text{CO}\cdot\text{CHMe}_2$  (Wallach, loc. cit.) derived from  $\Delta^1$ -isopropylcyclohexene. By the action of mag-

nesium methyl iodide on the cold *acid chloride*, b. p.  $86.5^{\circ}/23$  mm., of 1-methylcyclohexane-1-carboxylic acid (from the hypobromite oxidation, see above), 1-acetyl-1-methylcyclohexane can be prepared in relatively large quantities as a mobile oil, b. p.  $186.5-187^{\circ}$ ,  $d_4^{20}$  0.9178,  $n_D^{20}$  1.45484, possessing a strong camphor-like odour, and giving a semicarbazone, thick needles, m. p.  $186^{\circ}$  (Tarboureich,  $158^{\circ}$ ), and an oxime, small, lustrous needles, m. p.  $38-39^{\circ}$  (Tarboureich,  $45^{\circ}$ ). Reduction of the ketone by means of sodium in moist ethereal solution leads to 1-methyl-1- $\alpha$ -hydroxycyclohexane, b. p.  $87.5^{\circ}/13$  mm.,  $d_4^{20}$  0.9312,  $n_D^{20}$  1.47203, a thick, colourless oil, possessing a musty odour characteristic of pinacolyl alcohols; the phenylurethane has not been obtained crystalline. The elimination of water, by heating with zinc chloride, gives an 81% yield of a mixture of *hydrocarbons*, b. p.  $154-156.5^{\circ}$ ,  $d_4^{20}$  0.8270,  $n_D^{20}$  1.46083, which on oxidation by means of ozone leads to the same products as before.

The optical properties of the extracyclic pinacolins and pinacolyl alcohols described in this and preceding communications are tabulated, it being shown that all these compounds exhibit a negative exaltation.

W. S. N.

**Picryl Sulphide. The Binary System: Toluene-Picryl Sulphide.** A. ROCHE and V. THOMAS (*Compt. rend.*, 1923, 176, 586-589).—The picryl sulphide used, after recrystallisation from acetone, melted at  $213^{\circ}$  on the Maquenne block, and almost immediately resolidified, changed colour, and remelted again at  $234^{\circ}$ . In a m. p. tube, the temperatures were  $211^{\circ}$  and  $230.5^{\circ}$ , respectively. It explodes in the neighbourhood of  $300^{\circ}$ . The addition of toluene lowers the temperature of explosion, and it is also more intense. The two constituents of the binary mixture are miscible in all proportions in the fluid state, and no definite combination is formed. The eutectic melts at  $78.3^{\circ}$  and contains 86.5% of toluene. With mixtures of approximately this composition, a phenomenon of double supercooling was observed, the thermometer falling regularly to  $74.5^{\circ}$ , then rising to  $76.65^{\circ}$ , falling again to  $75.1^{\circ}$ , and finally rising to  $78.3^{\circ}$ . The cause of this anomalous behaviour was not ascertained.

G. F. M.

**Effect of Relative Positions of Hydroxyl and Amino-radicals in the Migration of Acetyl from Nitrogen to Oxygen.** L. CHAS. RAIFORD and HAROLD A. IDDLIS (*J. Amer. Chem. Soc.*, 1923, 45, 469-475; cf. A., 1920, i, 156; 1922, i, 931).—Additional evidence is given in support of the view that the migration of the acetyl group from nitrogen to oxygen, when an *o*-acetamidophenol is benzoylated by the Schotten-Baumann method, is probably general. With *p*-acetamidophenols under the same conditions, benzoylation does not cause migration of the acetyl group. This process thus furnishes a further means of distinguishing between *o*- and *p*-aminophenols. The following new compounds are described: 2:6-dibromo-4-acetamidophenyl acetate, m. p.  $172-173^{\circ}$ ; 2:6-dibromo-4-acetamidophenyl benzoate, m. p.  $168^{\circ}$ ; 2:6-dibromo-4-benzamidophenyl acetate, m. p.  $165^{\circ}$ ; 3-bromo-5-acetamido-*o*-tolyl

benzoate, m. p. 196°; 6-bromo-5-benzamido-o-cresol, m. p. 189°; 3-bromo-5-benzamido-o-tolyl acetate, m. p. 130°; 2:4-dibromo-6-acetamido-m-tolyl acetate, m. p. 145—146°; 2:4-dibromo-6-acetamido-m-cresol, m. p. 222°; 2:4-dibromo-6 acetamido-m-tolyl benzoate, m. p. 182—183°; 2:4-dibromo-6-benzamido-m-tolyl acetate, m. p. 179°; 2:6-dibromo-4-acetamido-m-cresol, m. p. 171°, and 2:6-dibromo-4-benzamido-m-tolyl acetate, m. p. 198—199°.

W. G.

**Acetomethylamidophenyl Acetate.** H. T. CLARKE (U.S. Pat. 1434429).—Acetomethylamidophenyl acetate is prepared by adding acetyl chloride beneath the surface of dimethylaminophenyl acetate contained in a bath at 190°.

CHEMICAL ABSTRACTS.

**Preparation of  $\beta$ -Naphthol-4-Sulphonic Acid.** GILBERT T. MORGAN and EVELINE JONES (*J. Soc. Chem. Ind.*, 1923, 42, 97—98r).—The preparation of  $\beta$ -naphthol-4-sulphonic acid from naphthalene-1-diazo-2-oxide-4-sulphonic acid, a commercially available product, is described. Sixty g. of the latter were heated with 900 c.c. of absolute alcohol in a reflux apparatus for about twenty-one hours and the resulting solution neutralised with barium carbonate. Alcohol was distilled off, the residual thick paste dissolved in water and the solution decolorised with animal charcoal, concentrated, and the residue dried over sulphuric acid.  $\beta$ -Naphthalene-1-azo- $\beta$ -naphthol-4-sulphonic acid, p-nitrobenzene-1-azo- $\beta$ -naphthol-4-sulphonic acid, and p-toluene-1-azo- $\beta$ -naphthol-4-sulphonic acid were prepared from the resulting barium  $\beta$ -naphthol-4-sulphonate, which was obtained as a hard, friable mass extremely soluble in water. The three azo-colours dyed on wool and silk in varying shades of red.

J. S. G. T.

**The 1:2-cycloHexanediols and o-Chlorocyclohexanol.** MARCEL GODCHOT (*Compt. rend.*, 1923, 176, 448—450).—The author finds for the 2-chlorocyclohexan-1-ol, as prepared by Detœuf (Thesis, Paris, 1920), or by Osterberg and Kendall (*A.*, 1920, i, 101), the m. p. 29°, when it has been carefully purified. It gives a phenylurethane, m. p. 97—98°, and with alcoholic potassium hydroxide the ether oxide described by Brunel (*A.*, 1905, i, 695). The chlorohydrin reacts with silver acetate to give the monoacetate of cyclohexan-1:2-diol, b. p. 122—124°/10 mm.,  $d^{15}_4$  1.091,  $n^{15}_D$  1.4685. This acetate on hydrolysis with aqueous-alcoholic potassium hydroxide gives the cyclohexanediol, m. p. 104°. The author considers that his results support the view of Böseken and co-workers (*A.*, 1921, i, 663) that the diol is a *cis-trans*-compound.

W. G.

**Rings through the Meta- and Para-positions of Benzene. A Study of certain Ethers of Resorcinol and m-Aminophenol.** W. C. WILSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 528—540).—An attempt has been made to produce ring structures through the meta- and para-positions of benzene by starting with various resorcinol ethers and with m- and p-aminophenol ethers, but in no instance was a meta- or para-ring obtained, such as might be expected from the reactions of compounds similar in

structure except for the presence of the oxygen atom or atoms. These results tend to confirm previous observations (cf. Mohr, A., 1919, ii, 229; and von Braun, A., 1913, i, 197; 1919, i, 40; 1920, i, 87), that a very definite kind and number of atoms are necessary for the formation of meta- and para-rings. Apparently, if there is any other reaction which has the slightest tendency to take place in preference to the formation of meta- and para-rings, such a reaction will occur. Thus when resorcinol di- $\gamma$ -cyanopropyl ether was reduced according to the method used by von Braun (*loc. cit.*) for *m*-xylylene dicyanide, not a trace of a ring compound was formed, but only the corresponding diamine in excellent yield. Further, by distillation of the monohydrochloride of this diamine, no ring compound was produced. Similarly, it was not possible to obtain a ring compound by treating resorcinol di- $\gamma$ -iodopropyl ether with a primary amine. The same ether and sodium under a variety of conditions gave no compound having a ring structure.

A number of resorcinol ethers have been prepared as follows. *Resorcinol di- $\beta$ -bromoethyl ether*, m. p. 94.5–95°, b. p. 166–167°/9 mm., was obtained by the interaction of ethylene bromide and sodium resorcinoxide in absolute alcohol. Attempts to prepare *resorcinol di- $\gamma$ -bromopropyl ether*, m. p. 67°, b. p. 204–206°/6 mm., by the same process gave principally a mixture of three other compounds, namely, *resorcinol  $\gamma$ -bromopropyl allyl ether*,

$\text{CH}_2\text{CH}:\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ ,  
m. p. 88–89°, *resorcinol diallyl ether*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2)_2$ , b. p. 166–168°/12 mm.,  $d_{20}^{20}$  1.1645,  $n_D^{20}$  1.5672, and a substance which was probably trimethylene  $\gamma$ -bromopropoxyphenyl allyloxyphenyl ether,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , m. p. 119–120°. *Resorcinol di- $\gamma$ -bromopropyl ether* was best prepared by heating together a mixture of resorcinol, potassium carbonate, and trimethylene bromide in aqueous acetone. From this ether, by the action of sodium iodide in aqueous acetone, *resorcinol di- $\gamma$ -iodopropyl ether*, m. p. 88–89°, was obtained. *Resorcinol di- $n$ -propyl ether*, b. p. 127–128°/12 mm.,  $d_{20}^{20}$  1.035,  $n_D^{20}$  1.5138, on bromination gave a *bromide*, m. p. 81°. The iodo-ether, when heated with *n*-amylamine, gave *resorcinol di- $\gamma$ -*n*-amylaminopropyl ether*, b. p. 249–252°/10 mm., isolated as its *dihydrochloride*, m. p. 287°. When boiled with sodium cyanide in aqueous alcohol, the iodo-ether was converted into *resorcinol di- $\gamma$ -cyanopropyl ether*, m. p. 31–32°, b. p. 236–237°/7 mm., which, when reduced with sodium in alcohol, yielded *resorcinol di- $\delta$ -aminobutyl ether*, b. p. 208–209°/7 mm.,  $d_{20}^{20}$  1.0589,  $n_D^{20}$  1.5315, giving a *monohydrochloride*, m. p. 233–234°, and a *dihydrochloride*, m. p. 248–249°. The monohydrochloride, when heated, decomposed, giving resorcinol, pyrrolidine, and *resorcinol mono- $\delta$ -aminobutyl ether*, m. p. 119–119.5°, b. p. 198–204°/8 mm., isolated as its *hydrochloride*, m. p. 159–161°. This amine, when dissolved in sodium hydroxide solution and shaken with *p*-nitrobenzoyl chloride, yielded *resorcinol di- $\delta$ -p-nitrobenzamidoethyl ether*, m. p. 123–124°.

When *m*-nitrophenol was heated with trimethylene bromide in the presence of sodium ethoxide, *m-nitrophenyl  $\gamma$ -bromopropyl ether*,

b. p. 186—188°/7 mm.,  $d_{20}^{25}$  1.513,  $n_D^{25}$  1.5700, was obtained, and this on reduction with stannous chloride and hydrochloric acid gave *m*-aminophenyl  $\gamma$ -bromopropyl ether, isolated as its hydrochloride, m. p. 114—115°. The free amine, when distilled, was decomposed, giving 6-aminochroman, b. p. 140—142°/7 mm.,  $d_{20}^{25}$  1.1549,  $n_D^{25}$  1.5944, which gave a hydrochloride, m. p. 158—160° (decomp.), a picrate, m. p. 182—183° (decomp.), a chloroplatinate, m. p. 224—225°, an acetyl derivative, and a benzenesulphonyl derivative, m. p. 148—148.5°. When the aminochroman was diazotised and the product coupled with  $\beta$ -naphthol, a brilliant red compound was obtained.

*m*-Nitrophenyl allyl ether, m. p. 31.5—32°, b. p. 136—137°/8 mm., was prepared from allyl bromide and *m*-nitrophenol, and on reduction yielded *m*-aminophenyl allyl ether, b. p. 120—122°/5 mm.,  $d_{20}^{25}$  1.0891,  $n_D^{25}$  1.5708, giving a hydrochloride, m. p. 145—146°, an acetyl derivative, and a benzenesulphonyl derivative, m. p. 83—83.5°.

Under similar conditions, starting with *p*-nitrophenol, there were prepared *p*-nitrophenyl  $\beta$ -bromoethyl ether, m. p. 64°; *p*-aminophenyl  $\beta$ -bromoethyl ether, m. p. 84°, and its hydrochloride, m. p. 196°. This amino-ether, when heated, gave no definite product.

W. G.

**Structure of Benzene.** MAURICE L. HUGGINS (*J. Amer. Chem. Soc.*, 1923, 45, 264—278).—The experimental data obtained by Hull (*Physical Rev.*, 1917, 10, 692) and by Debye and Scheerer (*A.*, 1917, ii, 437) indicate a structure for graphite composed of layers of closely packed benzene complexes of the type originally proposed by Körner. When similar closely packed layers in crystals of benzene and many of its derivatives are assumed, the dimensions of the benzene hexagon can be calculated from the crystallographic data. This has been done for the following substances, for which the half length,  $l$ , and the half width,  $w$ , are recorded: quinol,  $l=2.47$ ,  $w=2.14$ ; benzene,  $l=2.46$ ,  $w=2.19$ ; resorcinol,  $l=2.52$ ,  $w=2.08$ ; *p*-chloroaniline,  $l=2.47$ ,  $w=2.16$ ; pyrocatechol,  $l=2.62$ ,  $w=2.11$ ; *p*-dichlorobenzene,  $l=2.54$ ,  $w=2.13$ ; triphenylcarbinol,  $l=2.45$ ,  $w=2.13$ ; triphenylbenzene,  $l=2.44$ ;  $w=2.16$ ; tribenzylcarbinol,  $l=2.42$ ,  $w=2.11$ ; tribenzylsilicol,  $l=2.48$ ,  $w=2.16$ ; and triphenylmethane,  $l=2.47$ ,  $w=2.16$ . These values are very near to the values obtained for graphite,  $l=2.47$ ,  $w=2.14$  (Hull),  $l=2.52$ ,  $w=2.18$  (Debye and Scheerer). The arrangement of atoms, molecules, and electrons in the crystal has been partly determined.

J. F. S.

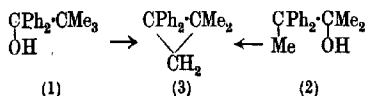
**The Phenylalanine Series. II. Synthesis of 3:4-Dihydroxyphenylethylamine.** E. WASER and H. SOMMER (*Helv. Chim. Acta*, 1923, 6, 54—61).—A new synthesis of 3:4-dihydroxyphenylethylamine was accomplished, starting from tyramine (*p*-hydroxyphenylethylamine). Tyramine was nitrated in aqueous suspension with nitric acid at 0—5°, and 3-nitro-4-hydroxyphenylethylamine nitrate separated. It crystallises in rosettes of yellow needles, m. p. 208° (decomp.). The free base forms microscopic prisms

or leaflets, varying from yellow to orange in colour, according to the solvent from which they are obtained, m. p.  $217^{\circ}$  (corr., decomp.). It is soluble in 200 parts of cold or 120 parts of hot water, and gives no colour reaction with Millon's reagent or with ferric chloride. The *hydrochloride* forms large, yellowish-brown leaves, decomposing, without melting, at  $214.5^{\circ}$  (corr.). The *chloroplatinate* forms golden-yellow needles decomposing at  $265^{\circ}$ , and the *picrate* deep yellow prisms, m. p.  $204^{\circ}$ . From the nitration liquor a small amount of 3:5-dinitro-4-hydroxyphenylethylamine was obtained, an orange-red, microcrystalline powder, decomposing at  $290^{\circ}$ . The *nitrate* crystallises in well-developed, yellow prisms, m. p.  $163^{\circ}$  (corr., decomp.), and the *picrate* forms a yellow, microcrystalline powder, m. p.  $196^{\circ}$ . It was identified by conversion into 3:5-dinitro-4-hydroxybenzoic acid. The reduction of 3-nitrotyramine was best accomplished with hydrogen in presence of platinum in dilute hydrochloric acid. 3-Amino-4-hydroxyphenylethylamine (aminotyramine) forms colourless, microscopic leaflets, m. p.  $145-147^{\circ}$  (corr.). It is soluble in 160 parts of cold or 50 parts of boiling water, from which it crystallises as a *monohydrate*, m. p.  $127^{\circ}$ . With Millon's reagent, it gives a yellow colour in the cold, becoming turbid and brown in the hot. Ferric chloride gives a deep reddish-violet colour, becoming yellow on addition of alkali, brownish-red with sodium acetate. It reduces an ammoniacal silver solution in the cold and Fehling's solution in the hot. The diazotised base gives a brownish-red colour with  $\alpha$ -naphthol. The base also gives the tyrosinase reaction with potato, but not so strongly as tyrosine. The *dihydrochloride* forms star- or feather-shaped groups of needles, m. p.  $305^{\circ}$  (corr., decomp.). This, when injected into the jugular vein of a dog caused a sharp rise of blood pressure. The *monopicrate* forms dark brown, pointed prisms, m. p.  $204.5^{\circ}$  (corr., decomp.); the *dipicrate* forms bright brownish-yellow leaflets, m. p.  $212^{\circ}$  (corr., decomp.). Attempts to obtain aminotyramine by decarboxylation of aminotyrosine gave a very poor yield.

3:4-Dihydroxyphenylethylamine was obtained by diazotising aminotyramine in sulphuric acid solution and running the diazo-solution into a boiling concentrated solution of copper sulphate. The *hydrochloride* forms groups of needles, m. p.  $237^{\circ}$  (corr., decomp.); the *picrate* forms brownish-yellow crystals, m. p.  $189^{\circ}$  (corr.). 3:4-Dihydroxyphenylethylamine gives a red colour with Millon's reagent, and a green colour, destroyed by excess of the reagent, with ferric chloride. It reduces an ammoniacal silver solution in the cold and Fehling's solution in the hot. E. H. B.

**Molecular Transposition in the Diphenyl- $\psi$ -butylcarbinol Series.** (MME) PAULINE RAMART (*Compt. rend.*, 1923, 176, 684-686).—The action of acetyl chloride and acetic anhydride on diphenyl- $\psi$ -butylcarbinol results in the formation of a chloro-compound and a hydrocarbon, the former having the constitution  $\text{CMePh}_2\text{-CMe}_2\text{Cl}$  (A., 1922, i, 34). The same hydrocarbon has now been obtained by the dehydration of diphenyl- $\psi$ -butylcarbinol (1), and the tertiary alcohol (2) by the action of heat in presence of

infusorial earth, and from the corresponding chloro-compounds by the action of pyridine in sealed tubes at 120°.



The alcohol (2) was obtained by the action of 2 mols. of magnesium methyl iodide on ethyl  $\alpha$ -diphenylpropionate, and the chloro-compounds were obtained by the action of thionyl chloride on the alcohols. The identity of the four hydrocarbons obtained and that obtained from the carbinol (1) by the action of acetyl chloride and acetic anhydride was proved by the identity of the chloro-compounds obtained from them by the action of hydrogen chloride at -10°, by the identity of the tribromides, m. p. 200° (with decomp.), obtained by the action of bromine, by their comparative indifference to acid or alkaline permanganate, and by the identity of their physical constants,  $d_4^{20}$  1.008,  $n_D^{20}$  1.5746. The hydrocarbon is therefore regarded as an intermediate product in the formation of the chloro-compound,  $\text{CMePh}_2\cdot\text{CMe}_2\text{Cl}$ , from diphenyl- $\psi$ -butylcarbinol, and as having the cyclopropane structure (3).

G. F. M.

**Ethers of Triphenylcarbinol.** BUECKHARDT HELFERICH, PAUL ELIAS SPIDEL, and WALTER TOELDTE (*Ber.*, 1923, 56, [B], 766-770).—Triphenylmethyl chloride reacts with alcohols in the presence of anhydrous pyridine at the atmospheric temperature or when warmed to give the corresponding ethers:  $\text{CPh}_3\text{Cl} + \text{R}\cdot\text{OH} = \text{R}\cdot\text{O}\cdot\text{CPh}_3 + \text{HCl}$ . Since the action proceeds in the presence of an excess of pyridine, it is particularly suitable for compounds which are sensitive towards acids. The ethers generally crystallise readily and appear to be adapted to the identification and possibly the purification of alcohols. They appear to be generally stable towards boiling alcoholic alkali, but are readily hydrolysed by dilute methyl-alcoholic hydrogen chloride at the atmospheric temperature to the alcohol and triphenylcarbinyl methyl ether. The introduction of the triphenylmethyl group is therefore serviceable for the protection of hydroxyl groups.

The following individual compounds are described: *triphenylmethyl isopropyl ether*,  $\text{Pr}^s\cdot\text{O}\cdot\text{CPh}_3$ , colourless needles, m. p. 113°; *triphenylmethyl propyl ether*, colourless plates or prisms, m. p. 55°; *triphenylmethyl cetyl ether*, colourless plates or prisms, m. p. 40-41°; *triphenylmethyl allyl ether*, colourless plates or prisms, m. p. 76°; *triphenylmethyl cyclohexyl ether*, colourless prisms, m. p. 103°; *triphenylmethyl hydroxyethyl ether*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CPh}_3$ , prisms or plates, m. p. 98-100°, the corresponding *bistriphenylmethyl ethylene ether*, prisms or plates, m. p. 185-186°; *triphenylmethyl  $\alpha$ -glycerol ether*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{CPh}_3$ , m. p. 92-94°; (1) *glycerol  $\alpha$ -bistriphenylmethyl ether*, small prisms, m. p. 170-171°; *pyrocatechol bistriphenylmethyl ether*, small plates, m. p. 206-208°; *pyrocatechol triphenylmethyl ether*, needles, m. p. about 258°

after darkening at  $245^{\circ}$ , which, however, is stable towards alcoholic hydrogen chloride, and hence, possibly, has a different constitution.  
H. W.

**Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXIX. Some Binary Systems of Triphenylmethane, Triphenylcarbinol, and Trimethylcarbinol with other Components.** ROBERT KREMANN, OTTO MAUERMANN, ROBERT MÜLLER II, and WILHELM RÖSLER (*Monatsh.*, 1923, 43, 321—333).—Previous examination of the system triphenylmethane-*m*-phenylenediamine afforded no evidence for the existence of a compound (A., 1922, i, 131). Repetition of the work confirms this; there is formed simply a eutectic at  $58^{\circ}$  and 4% of triphenylmethane. The latter with *o*-phenylenediamine gives a eutectic at  $76.5^{\circ}$  and 12.5% of triphenylmethane. With *m*-phenylenediamine, the hydrocarbon gives two liquid layers in the region 25—93% of triphenylmethane, the (constant) temperature of primary crystallisation being  $81^{\circ}$ . In the case of *o*-phenylenediamine, the same holds for the region 29—50% triphenylmethane ( $89^{\circ}$ ). 2:4-Dinitrophenol and triphenylmethane do not form a compound, but merely a simple eutectic at  $81^{\circ}$  (86% hydrocarbon). Triphenylmethane and triphenylcarbinol give a simple eutectic at  $78^{\circ}$  and 17% of carbinol. *o*-Nitrophenol, contrary to expectation (steric effects), behaves like its meta- and para-isomerides with trimethylcarbinol, a compound of the type 1 phenol+2 carbinol being formed in all three cases (corresponding with 51.6% carbinol) (cf. A., 1895, ii, 205; 1897, ii, 476).

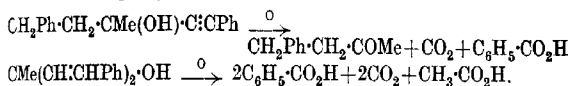
Triphenylcarbinol and 2:4-dinitrophenol form a simple eutectic only, at  $100^{\circ}$  and 19% carbinol. Trimethylcarbinol, on the other hand, gives, with this phenol, an equimolecular compound, m. p.  $89^{\circ}$  (28.7% carbinol). (Eutectic with phenol at  $85^{\circ}$  and 17% carbinol, that with triphenylcarbinol at  $20^{\circ}$  and 97%.)

Naphthalene does not form compounds with either trimethyl- or triphenylcarbinol, but only simple eutectics at  $19^{\circ}$  and 95% trimethylcarbinol and at  $69^{\circ}$  and 30% triphenylcarbinol, respectively. The fact that  $\alpha$ - and  $\beta$ -naphthylamines form compounds with these carbinols, whilst other amines previously examined do not (A., 1919, ii, 457, 458), cannot therefore be attributed to peculiar compound-forming properties of the naphthalene nucleus. E. E. T.

**Addition of Hydrogen to Acetylene Derivatives. X. Addition of Hydrogen to Diphenylphenylacetylenylcarbinol.** J. S. ZALKIND and (MILE) N. CICHANOVA (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 19—23; cf. A., 1916, i, 260).—Diphenylphenylacetylenylcarbinol,  $\text{CPh}_2\text{C}(\text{CPh}_2)\text{OH}$ , is reduced by the Sabatier method, using palladium as catalyst. No break in the rate of addition could be observed after the addition of 50% of the possible hydrogen, i.e., the process did not tend to stop with the formation of an ethylenic linking. Increase in the quantity of catalyst used accelerated the reaction,  $K$  increasing in the ratio 1:3.5:17 when the quantity of catalyst is increased as 1:2:5. The reduction

product was  $\alpha\gamma$ -triphenylpropan- $\alpha$ -ol, m. p. 85–87°. The action of bromine on the original carbinol was also investigated, and a dibromide, m. p. 99–100°, prepared. R. T.

**Addition of Hydrogen to Acetylene Derivatives. XI. Addition of Hydrogen to Alcohols having Two Triple Linkings.** J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 23–33; cf. A., 1916, i, 260).—Diphenylacetylenylmethylcarbinol,  $\text{CMe}(\text{C}:\text{CPh})_2\cdot\text{OH}$ , is reduced by the Sabatier method, using a palladium catalyst. As in previous cases (*loc. cit.*), addition of hydrogen leads to complete saturation of the acetylenic linkings, with no tendency to stop at the formation of ethylenic linkings. The reduction product is an oil,  $\gamma$ -hydroxy- $\alpha$ -diphenyl- $\gamma$ -methylpentane,  $d_4^{20}=1.0334$ ,  $n_D^{20}=1.55153$ , giving, from aqueous alcohol crystals, m. p. 51°, containing  $1\text{H}_2\text{O}$ . If the reduction process is stopped when half the possible hydrogen has been added, a mixture of unchanged carbinol, of saturated substance, and of  $\gamma$ -hydroxy- $\alpha$ -diphenyl- $\gamma$ -methyl- $\Delta^3$ -pentadiene,  $\text{CMe}(\text{CH}:\text{CHPh})_2\cdot\text{OH}$ , b. p. 210–212°/13 mm.,  $d_4^{20}=1.0638$ ,  $n_D^{20}=1.5580$ , is obtained. In order to prove that the product of reduction is not  $\delta$ -phenyl- $\beta$ -phenylacetylenylbutan- $\beta$ -ol,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{C}:\text{CPh}$ , the latter compound was synthesised from benzylacetone and magnesium phenylacetylenyl bromide. The oxidation of this compound leads to the production of benzylacetone and benzoic acid, whilst the oxidation of the diethylenic compound gives a mixture of benzoic and acetic acids, in the following way :

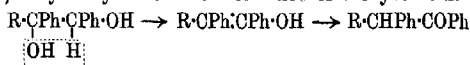


R. T.

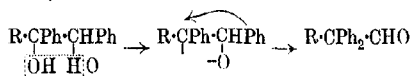
**Semipinacolic and Hydrobenzoinic Transpositions in the Alkylhydrobenzoin Series. Alkylhydrobenzoins with a Branched Chain. I. isoPropyl, isoButyl, and isoAmyl Chains.** M. TIFFENEAU and A. ORÉKHOFF (*Bull. Soc. chim.*, 1923, [iv], 33, 195–218).—The alkyl group in the alkylhydrobenzoins exercises a distinct and regular influence on the manner in which the dehydration of these substances occurs by the action of dilute or concentrated sulphuric acid. The results are interpreted in the light of Werner's ideas on variable affinity. When the affinity between the alkyl group and the rest of the molecule is strong, that of the tertiary hydroxyl is correspondingly weakened, and on dehydration it is eliminated with either the hydrogen contiguous to the secondary hydroxyl [vinyl dehydration (1)] or the hydrogen of the secondary hydroxyl [hydrobenzoin transformation (2)]. If, on the other hand, the affinity between the alkyl group and the rest of the molecule is feeble, as, for example, in the case of the isopropyl group, that of the tertiary hydroxyl is strengthened, and it is the secondary hydroxyl which is eliminated with the hydrogen of the tertiary hydroxyl [semipinacolic trans-

position (3)]. These reactions are expressed by the following schemes :

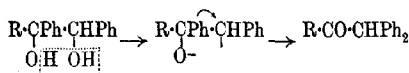
(1) Vinyl dehydration with formation of deoxybenzoins



(2) Hydrobenzoin transposition with formation of alkyl diphenyl acetaldehydes



(3) Semipinacolin transposition with formation of benzhydryl alkyl ketones



The dehydrating agent used also has a definite bearing on the sense of the reaction. Concentrated sulphuric acid augments the stability of the tertiary hydroxyl, or, if its affinity is weakened by the adjacent alkyl group, then it determines its elimination according to (1) above. Dilute sulphuric acid, on the other hand, has no effect on the stability of the hydroxyl but determines the aldehyde formation (2) by elimination of the hydrogen of the secondary hydroxyl. The following substances were prepared during the course of the research:  $\alpha\beta$ -Diphenyl- $\gamma$ -methylbutane- $\alpha\beta$ -diol (isopropylhydrobenzoin) prepared from benzoin and magnesium isopropyl bromide, forms colourless needles, m. p. 107–108°. On dehydration with cold concentrated sulphuric acid, the semipinacolin transformation occurs exclusively, with formation of  $\alpha\alpha$ -diphenyl- $\gamma$ -methylbutan- $\beta$ -one, colourless needles, m. p. 74–75°. For purposes of identification, this ketone was also prepared from diphenylacetaldehyde and magnesium isopropyl bromide, the resulting secondary alcohol,  $\alpha\alpha$ -diphenyl- $\gamma$ -methylbutan- $\beta$ -ol, b. p. 188–189°/16 mm., being converted into the ketone by oxidation with chromic acid. The isomeric ketone  $\alpha\beta$ -diphenyl- $\gamma$ -methylbutan- $\alpha$ -one (isopropyldeoxybenzoin), which was synthesised from deoxybenzoin and isopropyl bromide, formed needles, m. p. 70–71°, could not be found in the reaction mixture resulting from the dehydration of isopropylhydrobenzoin, and the vinyl dehydration (1) did not therefore occur at all. The dehydration of isopropylhydrobenzoin by treating with dilute sulphuric acid gave a mixture of the above  $\alpha\alpha$ -diphenyl- $\gamma$ -methylbutan- $\beta$ -one and  $\alpha\alpha$ -diphenylisobutaldehyde, a viscous liquid, b. p. 184–186°/15 mm.,  $d_4^{20}$  1.0522, produced according to the hydrobenzoin transformation (2). Its semicarbazone melts at 190–191°, and oxime at 93–94°. isobutylhydrobenzoin gives on dehydration with oxalic acid exclusively the substituted aldehyde,  $\alpha\alpha$ -diphenyl- $\gamma$ -methylbutaldehyde, a yellow oil, b. p. 195–196°/15 mm.,  $d_4^{20}$  1.035, forming a

*semicarbazone*, m. p. 147—148°, and an *oxime*, m. p. 153—154°. With concentrated sulphuric acid, vinyl dehydration occurs exclusively with formation of *isobutyldeoxybenzoin*. No trace of the isomeric ketone  $\alpha\alpha$ -diphenyl- $\delta$ -methylpentan- $\beta$ -one, m. p. 37—38°; *semicarbazone*, m. p. 168—169°, could be found in the mother-liquors. This ketone was synthesised by oxidation of  $\alpha\alpha$ -diphenyl- $\delta$ -methylpentan- $\beta$ -ol, a yellow oil, b. p. 185—195°/16 mm.  $\alpha\beta$ -Diphenyl- $\epsilon$ -methylhexan- $\alpha\beta$ -diol (*isoamylhydrobenzoin*) prepared from magnesium *isoamyl* bromide and benzoin, forms fine needles, m. p. 127—128°, and on dehydration with weak acids gives only the aldehyde (reaction 2),  $\alpha\alpha$ -diphenyl- $\delta$ -methylhexaldehyde, b. p. 205—210°/17 mm.; *semicarbazone*, m. p. 133—134°. With cold concentrated sulphuric acid, on the other hand, the reaction proceeds to the extent of about one-third according to the semipinacolin transformation and two-thirds vinyl dehydration. The former product,  $\alpha\alpha$ -diphenyl- $\epsilon$ -methylhexan- $\beta$ -one, forms a viscid oil, b. p. 205—210°/21 mm.; *semicarbazone*, m. p. 139—140°, and was identified by synthesis from  $\alpha\alpha$ -diphenyl- $\epsilon$ -methylhexan- $\beta$ -ol, a viscous liquid, b. p. 218—220°/26 mm., which was prepared from magnesium *isoamyl* bromide and diphenylacetaldehyde. The isomeric substance  $\alpha\beta$ -diphenyl- $\epsilon$ -methylhexan- $\alpha$ -one (*isoamyldeoxybenzoin*) forms small, colourless needles, m. p. 62—63°, and gives a *semicarbazone*, m. p. 127—128°. It was identified by synthesis from deoxybenzoin and *isoamyl* bromide. G. F. M.

**Addition of Hydrogen to Acetylene Derivatives. XII.**  
**Addition of Hydrogen to Diphenylbutinenediols and to the Acetyl Ester of Diphenylbutinenediol.** J. S. ZALKIND and (MLLE) Z. NEISCHTAB (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 34—42; cf. *ibid.*, 1914, 46, 1532; 1917, 49, 135).— $\alpha\delta$ -Diphenylbutinene- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CHPh}\cdot\text{C}\equiv\text{C}\cdot\text{CHPh}\cdot\text{OH}$  (A., 1914, ii, 258), is reduced by the Sabatier method, using a palladium catalyst. This compound exists in two stereoisomeric forms, melting at 140° and 102°, respectively, and both forms were examined. The velocity of reaction for both diminishes considerably after the triple bond has been changed to double, although it is still much greater than for ditertiary alcohols. By varying the quantity of catalyst in the order 1 : 2 : 3 : 5,  $K$  increased as 1 : 4 : 8 : 17. Whilst for both forms two space isomerides of the ethylenic reduction product are possible, only one form, m. p. 151°, is obtained from the less fusible isomeride, and two forms from the other, one m. p. 151—152°, but different from the one obtained previously, and the other an oil. The reduction of the diacetyl esters is next examined. This is much more rapid and complete than for the alcohols, and results in the production of  $\alpha\delta$ -diphenylbutane. No sharp break occurs with the formation of the ethylenic linking, but at saturation a rapid increase in the velocity of the reaction occurs, due to the reduction of the acetyl groups. By stopping the process when 25% of the possible hydrogen has been added on, the *diacetyl* ester, m. p. 97·5°, of the ethylenic reduction product, m. p. 152°, previously prepared, is obtained. R. T.

**Influence of Substitution in the Components on Equilibrium in Binary Solutions. XL. The Equilibrium in Binary Solutions of Acid Amides with Acid Anhydrides and with Acids.** ROBERT KREMANN, OTTO MAUERMANN, and VIKTOR OSWALD (*Monatsh.*, 1923, 43, 335—343).—Acetamide and benzoic anhydride form an equimolecular compound, m. p. about 84°, the eutectics lying at 68° (25% mol. of anhydride) and 38° (93% mol. of anhydride). The binary systems (1) acetamide-acetic anhydride, (2) benzamide-benzoic anhydride, and (3) benzamide-acetic anhydride were examined. A complete examination of (1) and (3) could not be made (i.e., beyond the limits 0—90% of acetic anhydride), owing to solubility effects, but a complete curve was obtained for (2), and shows the existence of a eutectic at 37° and 92% mol. of benzoic anhydride. Examination of the primary crystallisation curve for the system acetamide-acetic acid reveals the probable existence of an equimolecular compound (—5·5° and 50·5% acetic acid), this, with acetic acid, forming a eutectic at —16·5° and 69·5% acetic acid. Benzoic acid and benzamide form a eutectic at 78—79·5° (45·5—47·5% benzoic acid). Acetic acid and benzamide give a eutectic at —2° and 73% acid, benzoic acid and acetamide giving a eutectic at 38° and 56% acid. E. E. T.

**Production of Esters of Aromatic Acids [ $\gamma$ -Dialkylamino-propyl Aminobenzoates].** THE ABBOTT LABORATORIES (Brit. Pat. 191122).— $\gamma$ -Dialkylaminoalkyl esters of aromatic acids in general, and particularly  $\gamma$ -dialkylamino-*n*-propyl benzoates and aminobenzoates in which at least one of the alkyl groups is larger than an ethyl group, are obtained by heating the corresponding  $\gamma$ -halogeno-alkyl esters with a dialkylamine. The  $\gamma$ -dialkylamino-*n*-propyl aminobenzoates and their salts possess valuable local anæsthetic properties, and a specific example of their preparation is given:  $\gamma$ -bromo-*n*-propyl *p*-nitrobenzoate is heated for four hours at 60° with an equal weight of dibutylamine, the excess of amine is then removed by washing with water and distillation with steam, the residue is dissolved in benzene and extracted with dilute hydrochloric acid, the hydrochloride layer is separated and rendered alkaline, and the free base extracted with benzene. The  $\gamma$ -di-*n*-butylamino-*n*-propyl *p*-nitrobenzoate thus obtained is converted on reduction with iron and hydrochloric acid into the corresponding aminobenzoate, which is isolated as its hydrochloride or other suitable salt. *p*-Aminobenzoyl- $\gamma$ -di-*n*-butylamino-*n*-propanol hydrochloride is a crystalline solid, m. p. 151—152°. The hydrobromide melts at 143°, and the sulphate at 100°. Alternatively to the above method of preparation, the bromopropyl nitrobenzoate may first be reduced to  $\gamma$ -bromo-*n*-propyl *p*-aminobenzoate, m. p. 81·5°, and then afterwards condensed with dibutylamine. G. F. M.

**The Addition of Bromine to the  $\alpha$ - and  $\beta$ -Chloro- and Bromo-cinnamic Acids and their Esters.** J. J. SUDBOROUGH and GWYLYM WILLIAMS (*J. Indian Inst. Sci.*, 1923, 5, 107—118).—The addition of bromine in chloroform solution takes place much

more readily in diffused daylight than in the dark; the esters are more reactive than the free acids, and the  $\beta$ -halogenated compounds than the  $\alpha$ -halogenated compounds.  $\alpha$ -Bromocinnamic acid and  $\alpha$ -bromoallocinnamic acid and their methyl esters give the same  $\alpha\beta$ -tribromo- $\beta$ -phenylpropionic acid and *methyl  $\alpha\beta$ -tribromo- $\beta$ -phenylpropionate*, respectively, the former melting at 152–153°, and the latter at 47–48°. Similarly, the two stereoisomeric  $\beta$ -bromocinnamic acids and their methyl esters yield identical products,  *$\alpha\beta\beta$ -tribromo- $\beta$ -phenylpropionic acid*, m. p. 146–147° (decomp.), and *methyl  $\alpha\beta\beta$ -tribromo- $\beta$ -phenylpropionate*, m. p. 42–43°. The latter crystallises in tufts of slender needles. From the stereoisomeric  $\beta$ -chlorocinnamic acids, two different dibromides would theoretically be expected, but only one  *$\beta$ -chloro- $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid* was obtained. It formed colourless prisms from chloroform, m. p. 143–144°. Both  $\alpha$ -chlorocinnamic acids, however, gave a mixture of isomeric dibromides, and attempts to separate them were not successful. G. F. M.

**Products of the Distillation of  $\alpha$ -Truxillic Acid.** Isolation of a Fourth Truxillic Acid. HANS STOBBE and FRITZ ZSCHOCK (*Ber.*, 1923, 56, [B], 676–678).—The dry distillation of  $\alpha$ -truxillic acid yields *trans*-cinnamic acid, stilbene (which is probably derived secondarily from *trans*-cinnamic acid and not directly from  $\alpha$ -truxillic acid), a substance, m. p. 192–194°, which has not been definitely characterised,  $\gamma$ -truxillic anhydride, m. p. 189–190°, and  *$\eta$ -truxillic anhydride*,  $C_{18}H_{14}O_3$ , m. p. 287°, which is transformed into  *$\eta$ -truxillic acid*, m. p. 280°; the presence of benzaldehyde or truxone could not be detected.

[With FARRIS RAY.]—The dry distillation of *trans*-cinnamic acid yields mainly unchanged acid; in addition, styrene, stilbene, and indefinite products are formed. H. W.

**Investigations in the Phenylalanine Series. III. The Hydrogenation of Tyrosine.** E. WASER and E. BRAUCHLI (*Helv. Chim. Acta*, 1923, 6, 199–205).—Weinhagen attempted to hydrogenate tyrosine without success, and, although successful with phenylethylamine prepared from phenylalanine, failed to reduce synthetic phenylethylamine (*A.*, 1918, i, 107). The latter failure was probably due to the presence of some impurity which interfered with the catalytic hydrogenation, since the present authors, working with most carefully purified materials, have successfully hydrogenated tyrosine, using platinum black as the catalyst. Reduction was incomplete in alkaline or neutral solution but went completely in acid solution, best when exactly 2 mols. of hydrochloric acid per mol. of tyrosine was used. *Hexahydrotyrosine* crystallises from hot water in microscopic needles, m. p. 307° (corr., decomp.). It is soluble in about 25 parts of cold water. The hexahydrotyrosine from *l*-tyrosine is dextrorotatory,  $[\alpha]_D^{20} +13.18^\circ$ . The *hydrochloride*, which is extremely soluble in water, crystallises in leaflets or needles, m. p. 249° (decomp.). The *chloroplatinate*,  $(C_9H_{17}O_3N)_2 \cdot H_2PtCl_6 \cdot 3H_2O$ , forms bright yellow needles, m. p. 204° (decomp.). The *picrate* forms yellow needles, m. p. 196° (decomp.);

the *benzoyl* derivative,  $C_{16}H_{21}O_4N$ , forms colourless leaflets, m. p.  $186^\circ$  (corr.). The *phenylhydantoin* from hexahydrotyrosine crystallises in colourless needles, m. p.  $159-161^\circ$  (corr.). E. H. R.

**Investigations in the Phenylalanine Series. IV. The Rotation-Dispersion of Tyrosine and some of its Derivatives.** E. Waser (*Helv. Chim. Acta*, 1923, 6, 206-214).—Although tyrosine itself is levorotatory, most of its known derivatives are dextrorotatory. The rotations of many such derivatives have now been determined for a number of wave-lengths to discover whether any relation exists between the configuration of the asymmetric carbon atom and the rotation-dispersion such as was found by Karrer and Kaase in the glutaric acid series (A., 1919, i, 570). The following table gives the specific rotations at  $15^\circ$  for some of the principal lines:

| Substance.                                    | C 656.3        | 626            | D 589.3        | Hg 546.3       | E 527.0        |
|---|----------------|----------------|----------------|----------------|----------------|
| <i>L</i> -Tyrosine .....                      | $-10.27^\circ$ | $-11.30^\circ$ | $-12.30^\circ$ | $-13.76^\circ$ | $-14.61^\circ$ |
| <i>L</i> -3-Nitrotyrosine .....               | + 1.31         | + 2.36         | + 3.21         | + 3.97         | —              |
| <i>L</i> -3-Aminotyrosine .....               | — 3.69         | — 3.69         | — 3.61         | — 3.54         | —              |
| <i>L</i> -Tyrosine-3-diazonium chloride ..... | + 7.81         | + 9.50         | + 11.87        | —              | —              |
| <i>L</i> -3 : 4-Dihydroxyphenylalanine .....  | $-11.44$       | $-11.80$       | $-12.74$       | $-15.02$       | —              |
| <i>L</i> -3 : 5-Dinitrotyrosine ...           | + 7.81         | + 9.40         | + 11.45        | + 14.30        | + 16.48        |
| <i>L</i> -3 : 5-Diaminotyrosine...            | + 0.00         | + 1.02         | + 2.17         | + 1.18         | —              |
| <i>L</i> -Hexahydrotyrosine.....              | + 10.16        | + 11.83        | + 13.18        | + 15.70        | + 17.16        |

No conclusions of the kind expected are to be drawn from the results. The levorotatory compounds become more strongly *l*-rotatory the shorter the wave-length (tyrosine and 3 : 4-dihydroxyphenylalanine), whilst the *d*-rotatory compounds become more positive. In the cases of the two amino-derivatives there is very little change in rotation for different wave-lengths.

Natural tyrosine can be racemised readily by boiling in sodium hydroxide solution for about three days. *dl*-Tyrosine crystallises in star-shaped aggregates of extremely fine needles. The hydrochloride forms aggregates of long needles with no characteristic melting point. When given to a dog, *dl*-tyrosine is completely transformed and cannot be detected in the urine. E. H. R.

**The Wandering of Acyl Groups in the Cases of Phenolcarboxylic Acids (E. Fischer).** Syntheses of *p*-Di- $\beta$ -resorcylic Acid and *p*-Benzoylpyrogallolcarboxylic Acid. EUGEN PAOSU (*Ber.*, 1923, 56, [B], 407-424).—The cautious hydrolysis of penta-acetyl-*p*-digallic acid by cold, dilute ammonia led unexpectedly to the production of *m*-digallic acid (Fischer, Bergmann, and Lipschitz, A., 1918, i, 172), whereby a migration of the acyl group is involved (cf. A., 1908, i, 893; 1911, i, 875; 1913, i, 479). The constitution of many dipeptides, such as di- $\beta$ -resorcylic acid and gentisic acid, is rendered somewhat uncertain by this observation (cf. Bergmann and Dangschat, A., 1919, i, 273). The structure of *p*-di- $\beta$ -resorcylic acid is now confirmed by its synthesis, and it is established that the migration of aromatic acyl does not

take place with phenolcarboxylic acids of the type of  $\beta$ -resoreylic acid, or, in all probability, of gentisic acid.

It has been assumed previously that the wandering of aromatic acyl groups only takes place in phenolcarboxylic acids which contain the phenolic hydroxyl groups in the vicinal position to one another. As the result of a lengthy series of experiments the author has drawn the conclusion, however, that this view is incorrect and that the phenomenon is due to the influence of the carboxyl group which is most pronounced on the *p*-hydroxyl radicle. This influence is less marked when the carboxyl group is esterified, and is still less pronounced when a phenolic hydroxyl group is in the vicinal position; in the latter case, a migration of the acyl group is not observed.

2:4-Diacetoxybenzoic acid (cf. Bergmann and Dangschat, *loc. cit.*) is prepared by the action of acetic anhydride and pyridine on  $\beta$ -resoreylic acid, and is converted by phosphorus pentachloride in the presence of chloroform or by thionyl chloride into 2:4-di-acetoxybenzoyl chloride, a pale yellow liquid which solidifies when cooled to  $-20^\circ$ , b. p.  $170^\circ/12$  mm. (partial decomp.); the corresponding anilide crystallises in slender, lustrous needles, m. p.  $126-127^\circ$ . The action of 2:4-diacetylbenzoyl chloride and sodium hydroxide on sodium 4-hydroxy-2-acetoxybenzoate in the presence of aqueous acetone leads to the formation of triacetyl-*p*-di- $\beta$ -resoreylic acid,  $C_6H_3(OAc)_2 \cdot CO \cdot O \cdot C_6H_3(OAc) \cdot CO_2H$ , small, ill-defined prisms, m. p.  $151-153^\circ$  after softening at about  $146^\circ$ ; it is hydrolysed by cautious treatment with sodium hydroxide or ammonia to *p*-di- $\beta$ -resoreylic acid, microscopic, prismatic needles, m. p.  $206^\circ$  [ $211^\circ$  corr. (decomp.)], which differs from the corresponding ortho-compound mainly in its relative insolubility in water. It is re-converted by acetic anhydride and pyridine into triacetyl-*p*-di- $\beta$ -resoreylic acid. Short treatment of *p*-di- $\beta$ -resoreylic acid with diazomethane in the presence of ether yields the 4'-methyl ether of methyl *p*-di- $\beta$ -resoreyate,  $OMe \cdot C_6H_3(OH) \cdot CO \cdot O \cdot C_6H_3(OH) \cdot CO_2H$ , slender, lustrous needles, m. p.  $144-145^\circ$ , whereas more protracted treatment in the presence of acetone appears to yield a fully methylated product which has not been examined completely.

4-Benzoyloxy-2-acetoxybenzoic acid (cf. Bergmann and Dangschat, *loc. cit.*) is obtained in 93% yield by the method used in the preparation of triacetyl-*p*-di- $\beta$ -resoreylic acid; it is converted by diazomethane into methyl 4-benzoyloxy-2-acetoxybenzoate, hexagonal prisms, m. p.  $99-100^\circ$ , from which methyl 2:4-dihydroxybenzoate, colourless needles, m. p.  $121-122^\circ$ , is obtained by the action of 5*N*-ammonia.

The derivatives of 2:3:4-trihydroxybenzoic acid have been particularly examined, since migration of the acyl groups is to be expected if Fischer's hypothesis of the influence of vicinal hydroxyl groups is correct; such migrations are not, however, observed. 2:3:4-Triacetoxybenzoic acid, colourless prisms, m. p.  $164^\circ$  after previous softening, is prepared by the action of acetic anhydride and zinc chloride on 2:3:4-trihydroxybenzoic acid and is converted by cautious hydrolysis in an atmosphere of hydrogen into 4-hydroxy-

2:3-diacetoxybenzoic acid, long, colourless needles (+ H<sub>2</sub>O), m. p. (anhydrous) 157° after slight softening; the latter acid appears to be converted by boiling water into 3:4-dihydroxy-2-acetoxybenzoic acid, flat prisms, decomp. 192°. The diacetoxy-acid is transformed by diazomethane into methyl 2:3-diacetoxy-4-methoxybenzoate, rhombic platelets, m. p. 108°, which is hydrolysed to 2:3-dihydroxy-4-methoxybenzoic acid, long, colourless needles, decomp. 207—208°, identical with the substance prepared by Herzig and Pollak (A., 1904, i, 808) by the partial methylation of methyl 2:3:4-trihydroxybenzoate. 4-Hydroxy-2:3-acetoxybenzoic acid and benzoyl chloride yield 4-benzoyloxy-2:3-diacetoxybenzoic acid, aggregates of colourless, slender needles, m. p. 161—162°, which is hydrolysed by 5*N*-hydrochloric acid in the presence of glacial acetic acid to 2:3-dihydroxy-4-benzoyloxybenzoic acid, lustrous leaflets, decomp. 210—211°; re-acetylation of the latter acid with acetic anhydride gives 4-benzoyloxy-2:3-diacetoxybenzoic acid. 2:3-Dihydroxy-4-benzoyloxybenzoic acid is converted by diazomethane into methyl 4-benzoyloxy-2:3-dimethoxybenzoate, coarse, colourless crystals, m. p. 79—80°, from which 4-hydroxy-2:3-dimethoxybenzoic acid, microscopic, colourless, rhombic platelets, m. p. 154—155° after slight previous softening, is obtained by hydrolysis. H. W.

**The Reaction of Alcohols with Bromomethylphthalimide and its Use for the Separation and Identification of Alcohols.**

HARRIS H. HOPKINS (*J. Amer. Chem. Soc.*, 1923, 45, 541—544; cf. Pucher and Johnson, A., 1922, i, 549).—Bromomethylphthalimide reacts with certain alcohols under anhydrous conditions to give crystalline ethers, which can be used for the identification and separation of the alcohols. This procedure may be used for detecting the presence of methyl alcohol in dry acetone. The reaction does not proceed in the presence of moisture, as the bromomethylphthalimide is converted into hydroxymethylphthalimide before it can react with the alcohol. The following ethers are described: *Phthalimidomethyl methyl ether*, C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N·CH<sub>2</sub>·OMe, m. p. 118°; *phthalimidomethyl ethyl ether*, m. p. 86°; *phthalimidomethyl n-propyl ether*, m. p. 52—53°; *phthalimidomethyl isopropyl ether*, m. p. 92—93°; *phthalimidomethoxyacetic acid ether*, m. p. 185°; *phthalimidomethyl phenyl ether*, m. p. 171—172°; *triphtalimidomethyl glyceryl ether*, m. p. 174—175°. W. G.

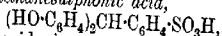
**Phenolsulphonophthalein and some of its Derivatives.**

W. R. ORNDORFF and F. W. SHERWOOD (*J. Amer. Chem. Soc.*, 1923, 45, 486—500).—In the preparation of phenolsulphonophthalein from the chloride of *o*-sulphobenzoic acid and phenol, the ordinary method of purification, by solution in sodium hydroxide and subsequent precipitation with acid, does not remove one impurity. This substance is soluble in the alkali hydroxide, but unlike the phthalein it is not soluble in cold aqueous sodium or ammonium hydrogen carbonate. This compound only contains about half as much sulphur as phenolsulphonophthalein, and is apparently

formed from it by the action of the excess of phenol. When the aqueous filtrates from the crude phenolsulphonephthalein were concentrated and then boiled with an excess of pure barium carbonate, *p*-hydroxybenzoylbenzene-*o*-sulphonic acid was obtained as its barium salt. This acid may also be prepared by heating ammonium *o*-sulphobenzoate with phenol for fifteen hours at 180–210°, and is obtained in the form of pink crystals containing 1H<sub>2</sub>O, or as a red, internal anhydride, which probably has the quinonoid structure  $O:C_6H_4:C \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ O \end{smallmatrix} SO_2$ . When heated at

135–140°, this acid loses water and gives phenolsulphonephthalein and the anhydride of *o*-sulphobenzoic acid. The phthalein prepared in this way is free from the impurity mentioned above.

As phenolsulphonephthalein is a coloured compound, it is represented by a quinonoid formula. Because it is the sulphonic acid derivative of benaurin, it is highly probable that dry phenolsulphonephthalein should be represented as an inner oxonium or carbonium salt. The crystallised, air-dried product always contains about 1.26% of water, which indicates that it is a solid solution of this inner salt and the quinonoid hydrate. Phenolsulphonephthalein gives an unstable *diammonium* salt, a *monoammonium*, a *sodium*, and a *disodium* salt. It also gives a *diacetate*, m. p. 165°, and a *dibenzoate*, m. p. 185–186° (decomp.). When heated with aniline for two hours at 140–150°, the phthalein gives *diphenylamine-sulphonephthalein*, a green compound. When pure phenolsulphonephthalein, suspended in water, is boiled with zinc dust, it gives a zinc salt from which, by decomposition with hydrogen sulphide, *dihydroxytriphenylmethanesulphonic acid*,



is obtained. This acid gives a *sodium* salt, and is very readily oxidised in the air to the sulphonephthalein.

When boiled with methyl alcohol containing 3% of hydrochloric acid, phenolsulphonephthalein gives, not an ester, but a colourless *monomethyl ether*, m. p. 178°, which resembles the methyl ether of phenolphthalein very closely in its properties and chemical behaviour. When heated for half an hour in a current of dry air at 170°, the colourless ether is converted into a red *methyl ether*, which, unlike the colourless ether, gives a stable *monoammonium* salt. Under similar conditions, a colourless *ethyl ether*, m. p. 171°, and a coloured *ether*, giving an ammonium salt, were obtained. Phenolsulphonephthalein, its salts, the coloured ethers, and diphenylaminesulphonephthalein are coloured and have the quinonoid structure, but the diacetate, the dibenzoate, and the colourless ethers are derivatives of the lactoid modification.

When tetrabromophenolsulphonephthalein is purified by crystallisation from glacial acetic acid it is colourless and has m. p. 279° (corr.). It has the lactoid, and not the carbinolsulphonic acid structure. Like phenolsulphonephthalein, it is tautomeric and gives coloured quinonoid and colourless lactoid derivatives. Its *hydrate*, its *diammonium*, *disodium*, and *monosodium* salts, and its *methyl ether* are coloured, and have the quinonoid structure. The

*diacetate*, m. p. 234°, and the *dibenzoate* are colourless and are derivatives of the lactoid form. The methyl ether gives an unstable *hydrochloride* and an *ammonium salt*. W. G.

**The Nitration of Benzaldehyde and the Monotropy of *o*-Nitrobenzaldehyde.** OSCAR LISLE BRADY and SAMUEL HARRIS (T., 1923, 123, 484—494).

**Syntheses of Coumarin- and Conifer-aldehydes.** H. PAULY and K. WÄSCHER (*Ber.*, 1923, 56, [B], 603—610).—Hydroxy-phenylacetaldehydes have hitherto been difficultly accessible substances, since their unusual tendency towards resinification under the influence of alkali hydroxide inhibits their preparation by alkaline condensation of hydroxyphenylaldehydes and acetaldehyde. A certain amount of success has been achieved by Tiemann by masking the hydroxyl group by using substances such as glucose, vanillin; it is not possible to use alkali for the removal of the glucose residue, but this can be effected with the aid of emulsin. A more convenient method is now described, which consists in masking the hydroxyl group by transforming it into the methoxymethoxy-residue,  $\text{OMe}\cdot\text{CH}_2\cdot\text{O}-$ ; the latter is ultimately removed by cautious and rapid treatment with very dilute acid.

*o*-Methoxymethoxybenzaldehyde (cf. Höring and Baum, A., 1909, i, 572) condenses with acetaldehyde in aqueous-alcoholic, alkaline solution at 60° to form *o*-methoxymethoxycinnamaldehyde,  $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$ , pale yellow crystals, m. p. 55°, b. p. 158—159°/3 mm., the yield being 37% of that theoretically possible. It is converted by short ebullition with acetic acid (50%) containing 0.3% of sulphuric acid into *o*-hydroxycinnamaldehyde, m. p. 133°. Similarly, *p*-methoxymethoxybenzaldehyde, b. p. 132—134°/9 mm. (cf. Höring and Baum, *loc. cit.*) is transformed into *p*-methoxymethoxycinnamaldehyde, a very viscous liquid which could not be caused to solidify, b. p. 158—160°/3 mm., and is converted into *p*-hydroxycinnamaldehyde, pale yellow needles, m. p. 134° (*semicarbazone*, m. p. 224°). 3-Methoxy-2-methoxymethoxybenzaldehyde,  $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$ , colourless plates, m. p. 56°, b. p. 128—130°/2 mm., is obtained in 11% yield by the action of chloromethyl ether on a suspension of the sodium derivative of *o*-vanillin in toluene. It is converted by acetaldehyde into 3-methoxy-2-methoxymethoxycinnamaldehyde, pale yellow, lustrous platelets, m. p. 91°, which is hydrolysed in the usual manner to 2-hydroxy-3-methoxycinnamaldehyde, pale yellow leaflets, m. p. 131° (*semicarbazone*, almost colourless crystals, m. p. 198° after softening at 195°). 3-Methoxy-4-methoxymethoxybenzaldehyde, colourless needles, m. p. 40°, b. p. 145—149°/4 mm., is transformed in the usual manner into 3-methoxy-4-methoxymethoxycinnamaldehyde, pale yellow needles, m. p. 77—78°, b. p. 165—167°/4 mm., which is further transformed into 4-hydroxy-3-methoxycinnamaldehyde, pale yellow needles, m. p. 82.5° (*semicarbazone*, pale yellow crystals, m. p. 218°); the sodium hydrogen sulphite compound is described. The aldehyde is slowly oxidised to vanillin on exposure to air.

H. W.

**Ring Closures from  $\gamma$ -Aryl-*n*-butyric Acids to Derivatives of 1-Ketotetrahydronaphthalene.** F. KROLLPFEIFFER and W. CHÄFER (*Ber.*, 1923, 56, [B], 620—632).—The conversion of phenyl-*n*-butyryl chloride into 1-ketotetrahydronaphthalene has been described by Kipping and Hill (T., 1899, 75, 146). Since, however, Schroeter (*Chem. Ztg.*, 1920, 759) has succeeded in effecting similar ring closures with the tetrahydronaphthyl-*n*-butyric acids without the employment of a condensing agent, the authors have endeavoured with partial success to avoid the indirect method through the chloride in the case of the simpler phenyl compounds.

The preparation of the requisite  $\gamma$ -aryl-*n*-butyric acids is effected by the condensation of the necessary benzenoid hydrocarbon with succinic anhydride in the presence of aluminium chloride and subsequent reduction of the ketonic acid thus produced by amalgamated zinc and hydrochloric acid; the latter action only gives satisfactory yields if carried out at the atmospheric temperature.

$\gamma$ -Phenyl-*n*-butyric acid is converted by treatment with concentrated sulphuric acid at the temperature of boiling water into 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 127°/13 mm. (semicarbazone, m. p. 217—220°), the yield being about 50% of that theoretically possible. Similarly,  $\gamma$ -*p*-tolyl-*n*-butyric acid is transformed into 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, colourless, crystalline aggregates, m. p. 32·5—33·5°,  $d_4^{25}$  1·0569,  $d_4^{20}$  1·072,  $n_D^{25}$  1·55168,  $n_D^{20}$  1·55674,  $n_D^{25}$  1·57160,  $n_D^{25}$  1·58479,  $n_D^{20}$  1·563. The corresponding semicarbazone crystallises in colourless, slender needles, m. p. 224—225°. The ketone is reduced by amalgamated zinc and concentrated hydrochloric acid to 2-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene, a colourless, mobile liquid, b. p. 224—226°,  $d_4^{25}$  0·9541,  $d_4^{20}$  0·950,  $n_D^{25}$  1·53318,  $n_D^{25}$  1·53719,  $n_D^{25}$  1·54907,  $n_D^{25}$  1·55897,  $n_D^{20}$  1·535 (cf. Schroeter, A., 1921, i, 861). It is converted by bromine in the presence of carbon disulphide into 2-bromo-1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, slender, colourless needles, m. p. 80·5°, which is transformed by boiling diethylaniline into a mixture of 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene and 7-methyl- $\alpha$ -naphthol, small, colourless needles, m. p. 109°, b. p. 158—159°/12 mm.

*p*-Ethylbenzoylpropionic acid, m. p. 98—99°, is converted successively into  $\gamma$ -*p*-ethylphenyl-*n*-butyric acid, colourless, lustrous leaflets, m. p. 69—70°, and 1-keto-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless liquid, b. p. 152—153°/12 mm.,  $d_4^{22}$  1·0556,  $d_4^{20}$  1·053,  $n_D^{22}$  1·55478,  $n_D^{22}$  1·55988,  $n_D^{22}$  1·57454,  $n_D^{22}$  1·58752,  $n_D^{20}$  1·559 (semicarbazone, colourless needles, m. p. 223—225°). 2-Ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene has b. p. 245—246°,  $d_4^{26}$  0·9499,  $d_4^{20}$  0·948,  $n_D^{26}$  1·53072,  $n_D^{26}$  1·53474,  $n_D^{26}$  1·54627,  $n_D^{26}$  1·55594,  $n_D^{20}$  1·534.

6 : 2 : 4-Dimethylbenzoylpropionic acid, m. p. 111—112°, yields  $\gamma$ -*m*-xyl-*n*-butyric acid, m. p. 71°, which is converted by concentrated sulphuric acid in poor yield into 1-keto-5 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, coarse prisms, m. p. 49—50°.

$d_4^{25}$  1.0654,  $d_4^{20}$  1.061,  $n_D^{15}$  1.55986,  $n_D^{15}$  1.56496,  $n_D^{15}$  1.57971,  $n_D^{15}$  1.59284,  $n_D^{20}$  1.563 (*semicarbazone*, slender, colourless needles, m. p. 234—235°). (The poor yield is due to the sulphonation of the acid; the sodium salt of sulpho-*m*-xylyl-*n*-butyric acid is described.) The ketone is more conveniently prepared from  $\gamma$ -*m*-xylyl-*n*-butyryl chloride either by the action of heat or, more rapidly, by means of aluminium chloride in the presence of light petroleum. It is reduced by amalgamated zinc and hydrochloric acid to 5:7-dimethyl-1:2:3:4-tetrahydronaphthalene, a colourless liquid, b. p. 250—252°/atmospheric pressure,  $d_4^{20}$  0.960,  $d_4^{21}$  0.9589,  $n_D^{21}$  1.53683,  $n_D^{21}$  1.54094,  $n_D^{21}$  1.55287,  $n_D^{21}$  1.56297,  $n_D^{20}$  1.541.

1:2:3:4-Tetrahydronaphthalene and succinic anhydride yield  $\beta$ -2-tetrahydronaphthoylpropionic acid, m. p. 121—122°, which is converted into  $\gamma$ -tetrahydronaphthyl-*n*-butyric acid, colourless crystals, m. p. 49—50°. The latter substance is transformed by concentrated sulphuric acid into 1-keto-octahydroanthracene, m. p. 46—47°, b. p. 202°/13 mm. (*semicarbazone*, m. p. 252—253°). 2-Bromo-1-keto-octahydroanthracene crystallises in colourless needles, m. p. 110°; it is converted by boiling diethylaniline into 1-keto-octahydroanthracene and 1-hydroxy-5:6:7:8-tetrahydroanthracene, a colourless powder, m. p. 124°, which becomes brown on exposure to air.

The condensation of naphthalene with succinic anhydride leads to the formation of a difficultly separable mixture of  $\beta$ -1- and -2-naphthoylpropionic acids.  $\beta$ -1-Naphthoylpropionic acid, m. p. 131—132°, is prepared by the action of heat on  $\alpha$ -naphthoyliso-succinic acid, decomp. 158°, which is obtained by condensing ethyl sodiomalonate with  $\alpha$ -naphthyl bromomethyl ketone in the presence of benzene and subsequent hydrolysis of the product. Attempts to effect ring closure with mixtures of  $\gamma$ -1- and -2-naphthyl-*n*-butyric acids did not lead to any decisive result (cf. Schäfer, *Diss.*, Marburg, 1922).

$\beta$ -*p*-Methoxybenzoylpropionic acid, m. p. 147—148°, is reduced to  $\gamma$ -*p*-methoxyphenyl-*n*-butyric acid, colourless leaflets, m. p. 59—60°. The latter acid is readily sulphonated by sulphuric acid, so that this reagent cannot be used for converting it into 7-methoxy-1-keto-1:2:3:4-tetrahydronaphthalene, which, however, is prepared by the action of heat or of aluminium chloride in the presence of light petroleum on  $\gamma$ -*p*-methoxyphenyl-*n*-butyryl chloride; it crystallises in colourless platelets, m. p. 60—61° (*semicarbazone*, m. p. 222—224° when rapidly heated).

$\beta$ -Benzoyl- $\alpha$ -methylpropionic acid,  $\text{CH}_3\text{Bz}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , colourless needles, m. p. 129—140°, is converted into  $\gamma$ -phenyl- $\alpha$ -methyl-*n*-butyric acid, b. p. 174°/15 mm. (*anilide*, slender, colourless prisms, m. p. 140°). Concentrated sulphuric acid transforms the latter acid into 1-keto-2-methyl-1:2:3:4-tetrahydronaphthalene, a colourless liquid, b. p. 132°/15 mm.,  $d_4^{20}$  1.0600,  $d_4^{20}$  1.061,  $n_D^{20}$  1.54669,  $n_D^{20}$  1.55154,  $n_D^{20}$  1.56542,  $n_D^{20}$  1.57764,  $n_D^{20}$  1.552; the *semicarbazone* crystallises in colourless leaflets, m. p. 199—201° when rapidly heated.

H. W.

**Halogenation. XXII. The Action of Bromine and Nitric Acid on Organic Compounds. Preparation of Nitrosyl Tribromide and the Formation of Tetrabromobenzoquinone.**

RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1923, 45, 480—482).—It has previously been shown (*A.*, 1916, i, 705) that chloropicrin and tetrachloro-*p*-benzoquinone are formed by the exhaustive action of aqua regia on organic compounds. It has now been found that bromine and nitric acid behave similarly on organic compounds, giving rise to tetrabromobenzoquinone and a mixture of bromonitro-derivatives of methane. A mixture of hydrobromic and nitric acids gives the same results, but in this case nitrosyl tribromide is formed in the first instance.

W. G.

**$\beta$ -Halogen-substituted Anthraquinone Compounds.** F. W. ATACK (U.S. Pat. 1434980).— $\alpha$ -Halogenanthraquinone derivatives are converted into the corresponding  $\beta$ -derivatives when heated at 200° (or lower for a longer period) with concentrated sulphuric acid; chlorination may be effected simultaneously in presence of a chlorine carrier, such as iodine, if necessary. Generally,  $\beta$ -bromo-derivatives can be produced from  $\alpha$ -bromo-derivatives, even in the presence of other substituents, such as sulpho-groups, and of aminogroups if in a different nucleus from the bromine.

CHEMICAL ABSTRACTS.

**The Stereoisomeric Forms of Menthone.** REGINALD SLATER LUGHESDON, HENRY GEORGE SMITH, and JOHN READ (*Proc. Roy. Soc. New South Wales*, 1922, 56, 170—175).—Four optically active menthones are theoretically capable of existence, and they may be respectively represented by the symbols *Dd*, *Ll*; *Ld* and *Dl*, where *d* and *l* indicate the optical effects of the 1-carbon atom and *D* and *L* are similarly used for the 4-carbon atom. Reasons are given for regarding the *l*-menthone obtained by the oxidation of natural *l*-menthol as having the *Ld* configuration, and the *d*- and *l*-isomenthones as being the *Dd* and *Ll* compounds, respectively. The optical effects of the two asymmetric carbon atoms would thus be opposed in the menthones and conjoined in the isomenthones. The catalytic hydrogenation of *dl*-, *d*-, and *l*-piperitones gave an inactive isomenthone, forming a sparingly soluble semicarbazone, m. p. 219—220°, and two highly active isomenthones having  $[\alpha]_D^{20} +58.33^\circ$  and  $-57.40^\circ$ , respectively. It is suggested that these substances belong to a type of partly racemic compounds, of which four are theoretically possible, namely, *Dd*, *Dl*; and *Ld*, *Ll*, representing 1-racemic isomenthones, and *Dd*, *Ld*; and *Dl*, *Ll*, representing 4-racemic isomenthones. Finally, two wholly racemic compounds are to be expected, *Dd*, *Ll*; and *Ld*, *Dl*, being *l*-menthone, and *i*-isomenthone, respectively.

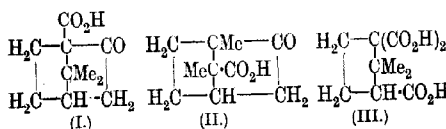
G. F. M.

**Two Definite Compounds of Nitrogen Peroxide and Camphor.** PAUL PASCAL and GARNIER (*Compt. rend.*, 1923, 176, 50—452).—A thermal analysis of the binary mixture, nitrogen

peroxide and camphor, shows the existence of two definite compounds, namely,  $5\text{N}_2\text{O}_4 \cdot 4\text{C}_{10}\text{H}_{16}\text{O}$ , m. p.  $-52^\circ$ , and  $2\text{N}_2\text{O}_4 \cdot 3\text{C}_{10}\text{H}_{16}\text{O}$ , m. p.  $-45.5^\circ$ . The former gives with nitrogen peroxide a series of solid solutions containing a maximum of 27% of camphor at  $-60^\circ$ . The binary system gives three eutectic mixtures, namely, a mixture, m. p.  $-60^\circ$ , containing 60.5% of nitrogen peroxide, a mixture, m. p.  $-55.5^\circ$ , containing 34.5% of nitrogen peroxide, and a mixture, m. p.  $-46.5^\circ$ , containing 26% of nitrogen peroxide.

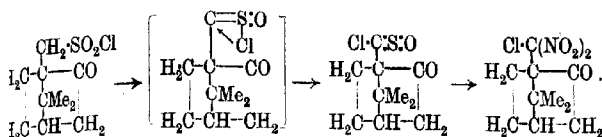
W. G.

**Transformation of *d*- and *l*-Camphorsulphonyl Chlorides into 10-*d*- and -*l*-Chlorosulphoxidocamphor.** The Constitution of Ketopinic Acid and of Reyckler's Camphorsulphonic Acid. E. WEDEKIND, D. SCHENK, and R. STRÜSSER (*Ber.*, 1923, 56, [B], 633—649).—It has been shown previously (Wedekind and Schenk, A., 1911, i, 190) that the action of strong tertiary bases on simple aromatic sulphonyl chlorides does not lead to the isolation of the expected "sulphens,"  $\text{CHAr} \cdot \text{SO}_2$ , which, however, are possibly formed as unstable intermediate products which break down into stilbenes and sulphur dioxide. In the hope of isolating such sulphens or derived substances containing sulphur, an examination has been made of more complex sulphonyl chlorides, for which purpose Reyckler's *d*-camphorsulphonyl chloride has been selected. The substance reacts readily with triethylamine (or pyridine), giving a mixture of equimolecular amounts of *d*-chlorosulphoxidocamphor,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{SCl}$ , and triethylammonium *d*-camphorsulphonate. The constitution of the former compound is mainly deduced from a study of its action on boiling dilute nitric acid, with which it yields sulphuric acid, a chlorodinitrocamphor (thus showing that the camphor skeleton is preserved practically unchanged in chlorosulphoxidocamphor and that the chlorine is united to a carbon atom), and *d*-ketopinic acid. *r*-Ketopinic acid has been obtained by Gilles and Renwick (T., 1897, 69, 1397, 1402) by oxidising pinene hydrochloride with fuming nitric acid, but its constitution has not previously been elucidated. Its



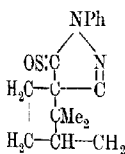
mode of formation renders one of the annexed formulae (I or II) possible, and the choice in

favour of I is rendered possible by the observation that it is oxidised to a tricarboxylic acid [carboxyapocamphoric acid (formula III)], which loses carbon dioxide when heated and yields apocamphoric acid. Since ketopinic acid is derived from camphor solely by alteration of the groups attached to the carbon atom 10, it follows that the substituents in chlorosulphoxidocamphor must also be present in this position, and the reaction may therefore be shown by the scheme:



Reychler's camphorsulphonic acid was regarded by the discoverer as an  $\alpha$ -compound, whereas subsequently Armstrong and Lowry (T., 1902, 81, 1469) brought forward evidence to show that the sulphonic acid group is attached to carbon atom 6 or 10, preference being finally accorded to the first possibility. The relationship of camphorsulphonyl chloride to ketopinic acid places beyond doubt the attachment of the acid residue to carbon atom 10, and this conception is in excellent agreement with the observed ability of camphorsulphonamide to yield an internal anhydride, since it indicates the production of a heterocyclic five-membered ring.

*d*-Camphorsulphonyl chloride reacts very energetically with triethylamine or pyridine, giving *d*-chlorosulphoxidocamphor, pale yellow, prismatic needles, m. p. 85°,  $[\alpha]_D^{25} + 58.28^\circ$  in benzene,  $[\alpha]_D^{25} + 136.2^\circ$  in chloroform. *l*-Chlorosulphoxidocamphor, prepared in a similar manner, has  $[\alpha]_D^{25} - 58.40^\circ$  in benzene and  $[\alpha]_D^{25} - 136.2^\circ$  in chloroform. *r*-Chlorosulphoxidocamphor is prepared by mixing equal quantities of its optically active components; it has m. p. 103.5°, and is shown to be a true racemate. The chlorine atom in these compounds is relatively firmly attached, and is not removed by silver oxide or by boiling aqueous silver nitrate solution. The protracted action of steam leads to the production of hydrogen chloride, sulphur dioxide, and sulphur, the latter being also prepared by the action of methyl-alcoholic ammonia. Reduction with stannous chloride gives an uncrystallisable substance containing sulphur.



It is remarkable that the chlorine atom is very readily removed by the action of phenylhydrazine, with the production of phenylhydrazine hydrochloride, a substance which the author terms *norcamphorylsulphoxide-N-phenylpyrazolone* (annexed formula), decomp. 155° after forming a clear, reddish-brown resin at about 80°. Chlorosulphoxidocamphor reacts with semicarbazide to give a chlorine-free product, m. p. 165–167° (decomp.), which could not be caused to crystallise.

The oxidation of the 10-chlorosulphoxidocamphors with nitric acid leads to the optically active 10-chloro-10:10-dinitrocamphors, m. p. 150.5° (decomp.),  $[\alpha]_D^{25}$  for which is respectively  $+52.06^\circ$  and  $-52.13^\circ$  in benzene and  $+55.47^\circ$  and  $-55.40^\circ$  in chloroform. The optically active *ketopinic acids* are simultaneously produced; they can also be obtained by the oxidation of the chlorosulphoxidocamphors with potassium permanganate or by the hydrolysis of the active 10-chloro-10:10-dinitrocamphors with water or, preferably, with water and calcium carbonate or slaked lime. *d*-Ketopinic acid has m. p. 234°,  $[\alpha]_D^{25} + 28.02^\circ$  in benzene, whereas the

constants of the *L*-isomeride are m. p.  $234^{\circ}$ ,  $[\alpha]_D^{25} - 27.67^{\circ}$  in benzene; *r*-ketopinic acid has m. p.  $234^{\circ}$ . The active ketopinic acids are converted into the corresponding *phenylhydrazones*, m. p.  $150.5^{\circ}$ , by the union of equal quantities of the antipodes, of which *r*-ketopinic acid phenylhydrazone, m. p.  $126.5^{\circ}$ , is prepared; this is identical with the product obtained from *r*-ketopinic acid derived from pinene hydrochloride [the m. p.  $146^{\circ}$  recorded for the inactive phenylhydrazone by Gilles and Renwick (*loc. cit.*) appears to be erroneous].

The chlorodinitrocampors are reduced by stannous chloride and hydrogen chloride in the presence of glacial acetic acid to the corresponding *ketopinonitriles*, m. p.  $197-198^{\circ}$ ,  $[\alpha]_D^{25} + 26.45^{\circ}$  and  $[\alpha]_D^{25} - 26.10^{\circ}$ , respectively, when dissolved in chloroform. Reduction appears to proceed along the lines indicated by the schemes  $R\cdot CCl(NO_2)_2 \rightarrow R\cdot C(NH_2)NOH + HCl, NH_2\cdot OH \rightarrow R\cdot CN$  and  $R\cdot CCl(NO_2)_2 \rightarrow R\cdot CCl(NH_2)_2 + HCl, NH_3 \rightarrow R\cdot CN$ , since both ammonia and hydroxylamine are also formed. The nitriles are hydrolysed by boiling sulphuric acid (50%) to the ketopinic acids, m. p.  $234^{\circ}$ .  
H. W.

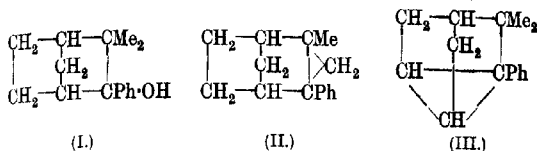
**Optically Active Heavy Metal Complexes.** I. LEFSCHITZ (*Rec. trav. chim.*, 1922, 41, 627-636).—Complex heavy metal salts and co-ordination compounds of hydroxymethylenecamphor are described. Earlier measurements of the rotatory dispersion of, for instance, aqueous solutions of tartaric acid in the presence of alkali and the salt of a heavy metal are open to the objection that such solutions may contain several optically active complexes, and that the observed experimental figures may be due to the superposition of the effects of their various components. The ferric, acid copper, normal copper, nickel, uranyl, aluminium, chromic, cobaltic, carbonatotetrammine and diethylenediamine-carbonato salts of hydroxymethylenecamphor are described. These compounds are soluble in organic media, so that the above objection presumably does not apply. The salts are all well-defined compounds with high rotatory powers, and, with the exception of the aluminium salt, all are brightly coloured. The rotatory dispersion of these compounds has been measured in the neighbourhood of their absorption bands, and has been found to be normal in some cases and anomalous in others. With the exception of the normal copper salt, however, none of these compounds exhibits the Cotton effect in the visible region of the spectrum, in spite of the fact that they all show characteristic selective absorption. The chromic salt is noteworthy in that its solutions in organic liquids exhibit strong dichroism and its rotatory dispersion curve shows both a maximum and a minimum in the visible region of the spectrum.

Similar ferric, chromic, and cobaltous derivatives of nitrocamphor are described.  
H. E.

***tert*-Phenylcamphenilol, its Conversion into Phenyl-pericycloapocamphane and Transformation into Phenylapocamphor.** MARIA BREDT-SAVELSBERG (*Ber.*, 1923, 56, [B], 554-561).—*tert*-Phenylcamphenilol has been prepared and its dehydration investigated since the process appeared to be of con-

siderable interest owing to the accompanying, enforced change of the carbon skeleton.

[With FRANZ TOUSSAINT.]—*tert*-Phenylcamphenilol (formula I), a colourless, viscous liquid, b. p. 122°/4 mm., 160–166°/13 mm.,



about 276°/atmospheric pressure (slight decomp.),  $d_4^{14}$  1.0717,  $n_D^{14}$  1.55518, is obtained by the action of magnesium phenyl bromide on camphenilone in the presence of ether (the corresponding optically active compound has  $[\alpha]_D +11.2^\circ$ ). It is a remarkably stable substance which is only slowly attacked by metallic sodium. It does not appear to yield a crystalline phenylurethane. The action of thionyl chloride or phosphorus pentachloride on it yields a mixture of the chloride and the hydrocarbon formed from the latter by loss of hydrogen chloride; treatment of the crude product with sodium phenoxide (or prolonged heating of *tert*-phenylcamphenilol with acetic anhydride at 170–180°) yields *phenyl- $\alpha$ -pericycloapocamphane*, a colourless, mobile liquid, b. p. 96–97°/5 mm.,  $d_4^{25}$  1.00609,  $n_D^{25}$  1.54710, which is stable towards permanganate. Its mode of formation renders possible the alternative formulæ II and III, of which the latter is preferred mainly on account of the observation that the inactive hydrocarbon is obtained from the optically active tertiary alcohol, whereas a substance of the constitution II is asymmetric, and would probably therefore be optically active.

Phenyl- $\alpha$ -pericycloapocamphane is converted by glacial acetic acid in the presence of a little concentrated sulphuric acid at 60–65° into *phenylapoisobornyl acetate*, b. p. 142–143°/4 mm.,  $d_4^{20}$  1.06888,  $n_D^{20}$  1.53003, and by anhydrous formic acid at 70° into *phenylapoisobornyl formate*, b. p. 127–128°/2 mm. The esters are hydrolysed with some difficulty to *phenylapoisoborneol* (annexed formula), a liquid, b. p. 145°,  $d_4^{12}$  1.0666,  $n_D^{12}$  1.55518. The latter substance is oxidised by chromic acid in glacial acetic acid solution to *phenylapocamphor*, b. p. 143°/55 mm.  $\text{CH}_2\text{CPh} \cdot \text{CO}_2\text{H}$  (semicarbazone, decomp. 199°) and by potassium permanganate in alkaline solution to *phenylapocamphoric acid* (annexed formula), decomp. 206°, which is transformed when distilled into the corresponding *anhydride*, m. p. 208–209°.

H. W.

Chemistry of the Phellandrenes. ERIC HURST, HENRY GEORGE SMITH, and JOHN READ (*Proc. Roy. Soc. New South Wales*, 1922, 56, 176–179).—*l*- $\alpha$ -Phellandrene gives as already recorded by Wallach and by Schreiner a mixture of two nitrosites, of which

the less soluble, or  $\alpha$ -nitrosite, was found to melt at 120–121°, agreeing with the figure given by Schreiner, but somewhat higher than that given by Wallach. Solutions of *l*- $\alpha$ -phellandrene  $\alpha$ -nitrosite in chloroform and in other organic solvents exhibited pronounced mutarotation, leading in every case to optical inversion in course of time. This observation has an important bearing on the discrepancy between the values for  $[\alpha]_D$  given by the above-mentioned authors, and on the application of the nitrosite reaction for the diagnosis of phellandrenes in essential oils. The initial value found for  $[\alpha]_D^{20}$  in freshly prepared chloroform solution was +137.7°. The  $\beta$ -nitrosite of *l*- $\alpha$ -phellandrene also appears to exhibit somewhat similar changes. G. F. M.

#### Australian *Melaleucas* and their Essential Oils. VI.

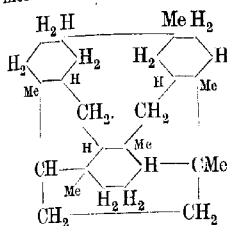
R. T. BAKER and H. G. SMITH (*Proc. Roy. Soc. New South Wales*, 1922, 56, 115–124).—The oil of *Melaleuca ericifolia* has the following constants:  $d^{15}_4$  0.8938,  $\alpha_D +13.3$ ,  $n^{20}_D$  1.4705. Between 168° and 190°, 52% distilled, consisting principally of *d*-pinene, *d*-limonene and dipentene, together with some cineol and terpineol; 26% distilled between 190° and 215°, consisting largely of terpineol. The remainder, about 15%, was mainly a sesquiterpene. The cineol was less than 10% of the total oil, and the oil cannot therefore replace the cajuput oil of commerce, which should contain at least 50% of cineol, and much less terpenes. The chief oxygenated constituent is terpineol, which imparts a more aromatic odour to the oil than that of cajuput oil. The oil of *M. Deanei* was only obtained in 0.7% yield from the leaves of the plant, and it was found to consist largely of *d*-pinene, together with about 15% of cineol and 4% of a high boiling alcohol, probably terpineol. The oil had the following characters:  $d^{15}_4$  0.8888,  $\alpha_D +22.7$ , and  $n^{20}_D$  1.4646. It has no economic value. G. F. M.

**The Occurrence of *l*-Phellandrene in the Oil of *Melaleuca acuminata*.** HENRY G. SMITH (*Proc. Roy. Soc. New South Wales*, 1922, 56, 159–161).—The oil of *Melaleuca acuminata* has the following characters:  $d^{15}_4$  0.8935,  $\alpha_D -12.8$ ,  $n^{20}_D$  1.4690, acid value 1.1, saponification value 4.5, saponification value after esterification 21.2, cineol content 43.7%. Thirty per cent. distilled between 165° and 170°, and 62% between 170° and 190°. After separation of the cineol as phosphate, the residual terpenes distilled to the extent of 80% between 166° and 172°. The chief constituent was apparently *l*-phellandrene, which was identified by its nitrosite. It is probable that this *l*-phellandrene will be found not to be identical with the *l*-phellandrene occurring in the oils of species of the "peppermint group" of eucalypts. G. F. M.

**The Constituents of Indian Turpentine from *Pinus longifolia*, Roxb.** II. JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU (*T.*, 1923, 123, 549–560).

**Composition of Caoutchouc.** MAITLAND C. BOSWELL [with A. HAMBLETON, R. R. PARKER, and R. R. McLAUGHLIN] (*Trans. Roy. Soc. Canada*, 1922, 16, III, 27–47).—The reactions used in

the investigation of the constitution of caoutchouc have been too drastic, and have given misleading indications of a fairly simple molecule. The earlier work is reviewed and certain new derivatives



are described. On the result of these researches a new formula (appended) is suggested which, it is claimed, adequately expresses the whole of the facts. Oxidation of caoutchouc dissolved in carbon tetrachloride by aqueous hydrogen peroxide yields a white, gummy mass,  $C_{30}H_{48}O_8$ , which readily undergoes atmospheric oxidation to a compound,  $C_{25}H_{40}O_2$ ; this compound can also be obtained by

the atmospheric oxidation of the pasty compound,  $C_{25}H_{40}O$  which is produced by the action of cold aqueous potassium permanganate on a solution of deresinised caoutchouc in carbon tetrachloride. Another compound isolated from the hydrogen peroxide reaction product had the composition  $C_{16}H_{24}O$ . By the action of iodine and aqueous hydrogen peroxide on caoutchouc dissolved in carbon tetrachloride a compound,  $C_{23}H_{40}O_8I$ , was obtained. Atmospheric oxidation of thinly sheeted deresinised caoutchouc in sunlight gave a tough, rubbery substance,  $C_{10}H_{16}O$ , and a brittle, transparent mass,  $C_{25}H_{40}O_2$ , which were separable by making use of the solubility of the former in carbon disulphide. Structural formulæ are given showing the relationship of these products with the parent caoutchouc (see also *J.S.C.I.*, 1923, 42, 63A).

D. F. T.

**Amber.** A. TSCHIRCH, E. AWENG, C. DE JONG, and E. S. HERMANN (*Helv. Chim. Acta*, 1923, 6, 214—225; cf. Tschirch and Aweng, A., 1895, i, 384).—A chemical comparison has been made of the two forms of amber, succinite and gedanite. The material was extracted with alcohol, the soluble portion again extracted with light petroleum, and the insoluble portion dissolved in ether. By extracting the ethereal solution with ammonium carbonate solution, two *succinoxyabietic acids* were obtained, that from succinite having the composition  $C_{20}H_{30}O_4$ , m. p. 122°, and that from gedanite,  $C_{19}H_{28}O_4$ , m. p. 120°. It is suggested that these may be homologues; they are present to the extent of about 0.5% in the amber. They are monobasic acids. By extracting the above ethereal solution next with sodium carbonate solution there was obtained a solution of *succinoabietinolic acid*,  $C_{40}H_{60}O_5$ , the composition being the same from both forms of amber. This also is a monobasic acid, and is present to the extent of 12%. These acids may be formed by autoxidation of resinic acids of the type of abietic acid,  $C_{20}H_{30}O_2$ . When the extract soluble in light petroleum is treated with 5% sodium hydroxide solution, a residue is left which after purification has the composition  $C_{40}H_{60}O_2$  and is termed *succinoabietinol*; it is present to the extent of 6%. Distillation of the alkaline solution with steam yielded about 0.2% of *d*-borneol, and from the alkaline solution addition of acid precipitates a new

monobasic acid, *succinosilvinic acid*,  $C_{22}H_{36}O_2$ , m. p.  $104^\circ$ , present to the extent of about 4%. The portion of amber insoluble in alcohol when hydrolysed with alkali gives succinic acid, about 2%, and a *succinoresinol*,  $C_{17}H_{20}O$ , about 3% on the original amber. The latter is undoubtedly the alcohol with which the succinic acid is combined. The trace of sulphur which is present in succinite but not in gedanite is associated with the succinoresinol. The remainder of the portion of the amber insoluble in alcohol, the *succinoresen*, which forms 65% of the whole in both succinite and gedanite, has m. p.  $324^\circ$ , and is quite indifferent to alkalis. It has the composition  $C_{22}H_{36}O_2$  and by distillation in a vacuum gives a mixture of phenols and terpenes. The possibility of the formation of the above constituents of amber from the resinic acids such as abietic acid found in recent conifer resins is discussed.

E. H. R.

**Studies of the Glucosides. II. Arbutin.** ALEXANDER KILLEN MACBETH and JOHN MACKAY (T., 1923, 123, 717—724).

**Tannins. II. Chinese Tannin.** P. KARRER, HARRY R. SALOMON, and J. PEYER (*Helv. Chim. Acta*, 1923, 6, 3—36).—E. Fischer considered Chinese tannin to be practically identical with penta-*m*-digalloyl-glucose (A., 1919, i, 87, 278). It is now shown, however, that the tannin is not a uniform substance, but can be separated by a suitable process into fractions differing considerably in rotatory power. The fractionation was accomplished by precipitating an aqueous solution of the tannin with aluminium hydroxide. The latter first dissolves in the tannin solution, but after a short time a precipitate appears, a compound of tannin and alumina, the nature of which is not yet understood. The compound was decomposed with acid in the cold, and the tannin extracted with ethyl acetate. The tannin first precipitated had the lowest rotatory power, the last had the highest. After a series of about eighty fractionations, the extreme fractions had rotations of  $+30^\circ$  and  $+157^\circ$ , respectively, in water, and  $+40.6^\circ$  and  $+51.5^\circ$  in pyridine. Similar results were obtained with different commercial samples of tannin and with samples extracted from the galls with acetone.

When the fractions having  $[\alpha]_D +80^\circ$  and above were treated with glacial acetic acid and hydrogen bromide at the ordinary temperature, they gave a 1-bromotetra(1-galloyl)glucose, a substance difficult to purify, which was readily converted by acetyl bromide into 1-bromotetra(triacetyl(1-galloyl)-glucose,  $C_{38}H_{51}O_{34}Br$ , an amorphous substance,  $[\alpha]_D +59.5^\circ$  in acetone. This was identical with a substance obtained in an exactly similar manner from synthetic penta(triacetyl(1-galloyl)-glucose, this product having  $[\alpha]_D +58.83^\circ$ . When warmed with sodium acetate and acetic anhydride, the above compound gave tetra(triacetyl(1-galloyl)-1-acetylglucose,  $C_{34}H_{42}O_{15}(OAc)_4$ . This is a white, amorphous substance; the specimen from the high rotating tannin fraction had  $[\alpha]_D +44.3^\circ$  in acetone, sinters from  $110^\circ$ , m. p.  $130$ — $135^\circ$ ; the sample from synthetic penta(triacetyl(1-galloyl)-glucose had  $[\alpha]_D +44.6^\circ$  and a

similar m. p. When treated with methyl alcohol and silver carbonate, bromo-1-tetra(triacetylgalloyl)-glucose gave tetra(triacetylgalloyl)- $\beta$ -methylglucoside,  $C_{55}H_{61}O_{33} \cdot OMe$ ,  $[\alpha]_D +31.8^\circ$  in acetone (from tannin) and  $+31.5^\circ$  (synthetic). Further, this methylglucoside was proved identical with that prepared from  $\beta$ -methylglucoside and triacetylgalloyl chloride, which had  $[\alpha]_D +32.9^\circ$ . On the other hand, tetra(triacetylgalloyl)- $\alpha$ -methylglucoside from  $\alpha$ -methylglucoside and triacetylgalloyl chloride had  $[\alpha]_D +42.3^\circ$  in acetone.

The above observations establish conclusively that the higher rotating fractions of Chinese tannin are derived from a penta-galloylglucose. The variations among the higher rotating fractions must be due to variations in the number and disposition of the depsidic galloyl groups present as digalloyl residues. The yield of tetra(triacetylgalloyl)-1-acetylglucose from any particular tannin fraction may be regarded as practically quantitative; hence the weight of this compound obtained gives a quantitative estimate of the number of gallic acid residues originally present. The mean number found for the different fractions was between 8 and 9 gallic acid residues per mol. of dextrose. Probably the different fractions contain from octa- to deca-galloylglucoses.

The lower rotating tannin fractions gave 1-bromotetra(triacetylgalloyl)-glucose and other derivatives differing markedly in rotatory power from those derivatives obtained from penta(triacetylgalloyl)-glucose. These fractions probably contain impurities besides the higher galloylated glucoses. It is concluded that Chinese tannin is a mixture of closely related galloylated glucoses, and that this complexity is the cause of its colloidal character. The pure substances must be very sparingly soluble in water, but the mixture forms colloidal supersaturated solutions. The living organism here makes use, as in the case of albumin, of the property possessed by insoluble substances of forming colloidal solutions in admixture with other substances of closely related structure.

E. H. R.

**Structure and Formation of Humic Acids and Coal.** J. MARCUSSE (Z. angew. Chem., 1923, 36, 42—43; cf. A., 1921, ii, 590; 1922, i, 437).—The absence of furan derivatives from, and the presence of benzene derivatives among, the products of the oxidation under pressure of humic acids furnishes no evidence whatever for the absence of furan nuclei in these substances, or for a benzene structure, since in the first place furan derivatives would not remain undecomposed under the conditions of the oxidation, and, secondly, benzene derivatives are obtained under similar conditions from cellulose and similar substances which certainly do not themselves possess a benzene structure. Eller's synthesis of humic acids by the oxidation of phenols with permanganate likewise furnishes no proof of a hydroxyquinonoid structure, since the boiling nitric acid used to obtain the nitro-compound, which was similar to the nitro-derivatives of the humic acids, would have oxidised the quinone nuclei, just as benzo-

quinone is converted by oxidising agencies into maleic acid, of which the anhydride is actually a furan derivative. The formation of chloranil by the oxidation of humic acids with potassium chlorate and hydrochloric acid can equally well have originated from a difuran derivative. With regard to the formation of coal, the humic acids originating from wood are converted by loss of carbon dioxide and water into pyrohumic acid and pyrohumic ketone, which, together with bitumen, cellulose, lignin, and mineral matter form brown coal. This is then converted by heat and pressure into ordinary coal and anthracite, and the synthetic production can be carried out by heating brown coal in a light mineral oil at 300° for twelve hours in a closed tube. The product is black, and shows all the properties of coal, being, unlike the original material, insoluble in molten alkali hydroxide, and giving no lignin reaction with dilute nitric acid. The synthetic coal differed from the natural product only in the absence of the asphaltic substances, the carboides, which are formed in nature from the waxy constituents of brown coal, and to which the lustre of the coal is due.

G. F. M.

#### Benzopyronesulphonic Acids and Coumarinmercaptans.

MARGARETE KRÜGER (*Ber.*, 1923, 56, [B], 480—488).—4:7-Dimethylcoumarin-6-sulphonic acid, colourless, slender needles, m. p. above 285° after previous darkening, is obtained by the addition of 4:7-dimethylcoumarin to sulphuric acid containing 20% of sulphur trioxide at 0° and heating the mixture at 80° after solution has become complete at the atmospheric temperature; the *sodium*, *potassium*, and *ammonium* salts are described. The dry sodium salt is transformed by phosphorus pentachloride at 160—170° into 4:7-dimethylcoumarin-6-sulphonyl chloride, large, colourless prisms, m. p. 175°, which is converted by ethyl alcohol into ethyl 4:7-dimethylcoumarin-6-sulphonate, lustrous needles, m. p. 172°. The sulphonyl chloride is reduced by zinc dust in the presence of alcohol to 4:7-dimethylcoumarin-6-thiol, small needles, m. p. 255°, the *mercury* and *lead* derivatives of which are described.

In a similar manner, 4-methylcoumarin-6-sulphonic acid (cf. Harnisch, *Diss.*, Berlin, 1911) is transformed into 4-methylcoumarin-6-sulphonyl chloride, pale yellow rhombs, m. p. 137°, ethyl 4-methylcoumarin-6-sulphonate, colourless, lustrous needles, m. p. 151—152°, and 4-methylcoumarin-6-thiol, pale yellow, rhombic prisms, m. p. 180—181°.

4:6-Dimethylcoumarin-8-sulphonyl chloride crystallises in long, colourless needles, m. p. 179°, and is reduced with some difficulty to 4:6-dimethylcoumarin-8-thiol, colourless needles, incipient decomp. 246° (the *mercury* and *lead* derivatives are described). Ethyl 4:6-dimethylcoumarin-8-sulphonate forms lustrous needles, m. p. 182°.

3:4:7-Trimethylcoumarin is only slowly converted by sulphuric acid containing 50% of sulphur trioxide at 100° into 3:4:7-trimethylcoumarin-6-sulphonic acid, m. p. above 300°, the *sodium*, *lead*, and *potassium* salts of which are described. 3:4:7-Tri-

*methylcoumarin-6-sulphonyl chloride* crystallises in short, thick needles, m. p. 214°.

7-Methoxy-4-methylcoumarin is transformed into the corresponding *sulphonic acid*, a colourless, crystalline mass, under the same conditions as is 4:7-dimethylcoumarin. *Sodium 7-methoxy-4-methylcoumarin-6-sulphonate*, needles, and the corresponding *potassium* and *barium* salts are described. The sodium salt is converted by phosphorus pentachloride at 180° into *7-methoxy-4-methylcoumarin-6-sulphonyl chloride*, lustrous rhombs, m. p. 201°, which is further transformed into *ethyl 7-methoxy-4-methylcoumarinsulphonate*, needles or leaflets, m. p. 199°, and *7-methoxy-4-methylcoumarin-6-thiol*, small leaflets, m. p. 178° (the *mercury*, *lead*, and *sodium* compounds are described).

The coumarinthiols resemble the coumarins in their behaviour towards bromine; thus 4:7-dimethylcoumarin-6-thiol gives the corresponding *dibromide*,  $C_{11}H_{10}O_2SBr_2$ , long needles, m. p. 271°, which is readily decomposed by water into the thiol and bromide.

Chromone is not sulphonated at 70–80° by sulphuric acid containing 50% of sulphur trioxide. Under closely similar conditions, 2:3-dimethylchromone is transformed into 2:3-dimethylchromone-6-sulphonic acid,  $SO_3H \cdot C_6H_3$   $\begin{smallmatrix} \diagup CO \cdot CMe \\ | \\ O \cdot CMe \end{smallmatrix}$ , a colourless mass which

does not melt at a definite temperature. The corresponding *sodium salt* (+4H<sub>2</sub>O) and *lead salt* (+2H<sub>2</sub>O) are described. Attempts to convert the sodium salt into the sulphonyl chloride were unsuccessful.

H. W.

#### Syntheses of Arylsulphone Derivatives of Naphthapyrones, Hydroxynaphthapyrones, and Trihydroxybenzopyrones.

JULIUS TRÖGER and RICHARD DUNKEL (*J. pr. Chem.*, 1922, [ii], 104, 311–334).—By a method previously described (Tröger and Bolte, A., 1922, i, 267), arylsulphone derivatives of naphthapyrones, hydroxynaphthapyrones, and trihydroxybenzopyrones have been prepared, and their fission by alkaline hydrolysis has been studied.

The arylsulphonylnaphthapyrones resemble, in their behaviour towards alkali hydroxides, the arylsulphonylcoumarins (Tröger and Bolte, *loc. cit.*). The action of moderately strong aqueous potassium hydroxide leads first, with disruption of the lactone ring, to the potassium salt of the coumarinic acid, from which, on acidification, the original pyrone is regenerated; if, however, the hydrolysis is continued, potassium carbonate and a styrene derivative are produced. Concentrated alkali hydroxide (30–40%) causes fission of the pyrone into the hydroxyaldehyde and the salt of the arylsulphonylacetic acid, the latter then passing into potassium carbonate and an arylmethylsulphone.

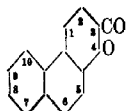
The hydroxyarylsulphonylcoumarins undergo fission more readily (*loc. cit.*) than the arylsulphonylcoumarins, but alkali carbonate and a styrene derivative are the sole products, the hydroxyaldehyde and the arylsulphonylacetic acid, or the arylmethylsulphone, not being formed. In contrast to this, the arylsulphonylhydroxynaphthapyrones are broken down by concentrated or

dilute alkali hydroxide into the relevant dihydroxynaphthaldehyde and an arylmethylsulphone.

Since trihydroxybenzaldehydes, which would be produced by the hydrolytic fission of arylsulphonyldihydroxycoumarins, are readily decomposed by alkali, the behaviour of the arylsulphonyldiethoxycoumarins has been studied, it being shown that whilst aqueous potassium hydroxide leads first to the salt of the coumarinic acid, acidification giving the original pyrone, by continued action neither an arylsulphone nor a styrol derivative is produced. The actual products have not yet been fully investigated.

It should be noted that the use of sodium ethoxide (Bilmmann, A., 1912, i, 461), for the fission of the pyrones described, is impracticable owing to their insolubility in alcohol. With the exception of the 3-arylsulphonyl-5:7-dihydroxycoumarins and the arylsulphonyldihydroxynaphthapyrones, all the compounds described show a pronounced fluorescence.

The reaction between  $\beta$ -naphthaldehyde, benzenesulphonyl-acetic acid (one-third of this as sodium salt), and acetic anhydride



commences in the cold, is completed on warming, and leads to 2-benzenesulphonyl-4:3- $\beta$ -naphthapyrone, pale yellow prisms, m. p. 253°. Similarly, acetic anhydride,  $\beta$ -naphthaldehyde, and *p*-toluenesulphonyl-acetic acid give 2-*p*-toluenesulphonyl- $\beta$ -naphthapyrone, pale yellow prisms, m. p. 275°, whilst the use of *p*-chlorobenzenesulphonyl-acetic acid leads to 2-*p*-chlorobenzenesulphonyl- $\beta$ -naphthapyrone, small, yellow prisms, m. p. 285°. The action of aqueous potassium hydroxide solution (10–30%) leads to known products (see above). 2:6-Dihydroxynaphthaldehyde condensed with benzenesulphonyl-acetic acid gives 8-acetoxy-2-benzenesulphonyl- $\beta$ -naphthapyrone, yellow leaflets, m. p. 246°, which on hydrolysis with 50% aqueous sulphuric acid gives 8-hydroxy-2-benzenesulphonyl- $\beta$ -naphthapyrone, flat, yellow prisms, m. p. above 270°. 8-Acetoxy-2-*p*-toluenesulphonyl- $\beta$ -naphthapyrone, flat, yellow prisms, m. p. above 265°, derived from *p*-toluenesulphonyl-acetic acid, gives 8-hydroxy-2-*p*-toluenesulphonyl- $\beta$ -naphthapyrone, m. p. above 270°, on hydrolysis; if *p*-chlorobenzenesulphonyl-acetic acid is used, 8-acetoxy-2-*p*-chlorobenzenesulphonyl- $\beta$ -naphthapyrone, a reddish-yellow, microcrystalline powder, m. p. about 274°, is produced, giving on hydrolysis 8-hydroxy-2-*p*-chlorobenzenesulphonyl- $\beta$ -naphthapyrone, thin needles of high m. p. 2:7-Dihydroxynaphthaldehyde, when condensed with the same three sulphonyl-acetic acids, gives 9-acetoxy-2-benzenesulphonyl- $\beta$ -naphthapyrone, yellow leaflets, m. p. 258°, 9-acetoxy-2-*p*-toluenesulphonyl- $\beta$ -naphthapyrone, yellow prisms, and 9-acetoxy-2-*p*-chlorobenzenesulphonyl- $\beta$ -naphthapyrone, yellowish-red prisms; hydrolysis gives, respectively, 9-hydroxy-2-benzenesulphonyl- $\beta$ -naphthapyrone, slender, yellow prisms, 9-hydroxy-2-*p*-toluenesulphonyl- $\beta$ -naphthapyrone, flat, yellow leaflets; and 9-hydroxy-2-*p*-chlorobenzenesulphonyl- $\beta$ -naphthapyrone, small, slender, yellowish-red prisms; all these compounds have high melting points. The action of aqueous alkali hydroxides on these hydroxy- or acetoxy-derivatives leads to known products (see above). The

condensation of pyrogallaldehyde with the same three acids gives 3-benzenesulphonyl-7:8-diacetoxycoumarin, small, white needles, m. p. 183°; 3-p-toluenesulphonyl-7:8-diacetoxycoumarin, white needles, m. p. 234°, and 3-p-chlorobenzenesulphonyl-7:8-diacetoxycoumarin, white needles, m. p. 223°, from which by hydrolysis 3-benzenesulphonyl-7:8-dihydroxycoumarin (+H<sub>2</sub>O), yellow prisms, m. p. 255°, 3-p-toluenesulphonyl-7:8-dihydroxycoumarin (+H<sub>2</sub>O), yellow needles, m. p. 258°, and 3-p-chlorobenzenesulphonyl-7:8-dihydroxycoumarin, yellow needles, m. p. 268° (decomp.), respectively, are obtained. From 2:4:5-trihydroxybenzaldehyde, 3-benzenesulphonyl-6:7-diacetoxycoumarin, white needles, m. p. 252°, 3-p-toluenesulphonyl-6:7-diacetoxycoumarin, white needles, m. p. 228°, and 3-p-chlorobenzenesulphonyl-6:7-diacetoxycoumarin, nodular aggregates of needles, m. p. 221°, are produced; hydrolysis gives, respectively, 3-benzenesulphonyl-6:7-dihydroxycoumarin, white needles of high m. p., 3-p-toluenesulphonyl-6:7-dihydroxycoumarin, yellow needles, m. p. 278° (decomp.), and 3-p-chlorobenzenesulphonyl-6:7-dihydroxycoumarin, small, yellowish-white needles of high melting point. From 2:3:5-trihydroxybenzaldehyde, 3-benzenesulphonyl-5:7-diacetoxycoumarin, white needles, m. p. 191°, 3-p-toluenesulphonyl-5:7-diacetoxycoumarin, white needles, m. p. 213°, and 3-p-chlorobenzenesulphonyl-5:7-diacetoxycoumarin, white needles, m. p. 211°, are obtained, giving on hydrolysis 3-benzenesulphonyl-5:7-dihydroxycoumarin, yellowish-brown, difficultly fusible needles, 3-p-toluenesulphonyl-5:7-dihydroxycoumarin, yellowish-white needles, m. p. 258—260° (decomp.), and 3-p-chlorobenzenesulphonyl-5:7-dihydroxycoumarin, very small, yellowish-white, difficultly fusible needles, respectively. The three last-mentioned dihydroxycoumarin derivatives, when alkylated by means of ethyl-alcoholic sodium ethoxide and ethyl iodide, give, respectively, 3-benzenesulphonyl-5:7-diethoxycoumarin, yellowish-white needles, m. p. 187°, 3-p-toluenesulphonyl-5:7-diethoxycoumarin, yellowish-white prisms, m. p. 227°, and 3-p-chlorobenzenesulphonyl-5:7-diethoxycoumarin, yellowish-white needles, m. p. 226°; the hydrolytic fission of these ethoxy-compounds requires the use of 20% aqueous alkali hydroxide, and has so far given, apart from recovered material, no recognisable product.

W. S. N.

**The Composition of "Chelalbines."** P. KARRER (*Helv. Chim. Acta*, 1923, 6, 232).—Fresh analyses of methylchelalbine (A., 1917, i, 349) give the empirical formula C<sub>21</sub>H<sub>17</sub>O<sub>4</sub>NMe, instead of C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>NMe. The chelalbines are therefore to be regarded as alkyl dihydrochelerethrines, their formation corresponding with that of the alkyl dihydroberberines by the action of Grignard's reagent on berberine.

E. H. R.

**Gel Formation in Quinine and Eucupine Solutions.** PETER RONA and MAKI TAKATA (*Biochem. Z.*, 1922, 134, 97—107).—The conditions for gel formation in quinine and eucupine solutions have been rigidly defined. The range of variation of conditions for quinine is very small, 1.5 c.c. of a 1% quinine hydrochloride

solution with 3 c.c. of a  $M/3$  phosphate mixture of  $P_H$  6.85 giving a stiff gel which crystallised after five to ten minutes. In the case of eucupine, gels of considerable stability are obtainable. Gel formation depends on the  $P_H$  values above 4.5 being inimical, on the particular buffering solution used, and on the concentration of the eucupine solution. The process of gelation can be followed by viscosity measurements, change of surface tension, and conductivity measurements. The gelation is reversible and the gel is suitable for Liesegang ring formation.

H. K.

### Indian Opium. III. The Meconic Acid Content of Indian Opium.

HAROLD E. ANNETT and MATHURA NATH BOSE (*Mem. Dept. Agric. India*, 1922, 6, 215—221).—The meconic acid was estimated in various samples of opium by the addition of calcium chloride solution to an aqueous extract of the opium and decomposition of the calcium salt by hydrochloric acid (A., 1922, ii, 791). The quantity of meconic acid is in all cases found to be roughly equivalent to that of the total alkaloids present, whereas the soluble sulphate content of the latex increases as the alkaloidal content diminishes, and it is concluded that the alkaloids are present as meconates only, the sulphate being present in a mineral form. The acid reaction of the latex is due to dissociation of the weakly basic alkaloids such as narcotine and papaverine. P. M.

### Preparation of Papaverine Nitrite.

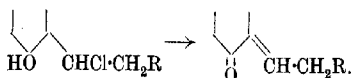
C. H. BOEHRINGER SOHN and HANS STENZL (Brit. Pat. 192298).—An aqueous solution of a papaverine salt is slowly treated with a 20% sodium nitrite solution either in the presence or absence of an organic solvent such as benzene. In the latter case, the oily reaction product consisting of a mixture of papaverine and papaverine nitrite is allowed to solidify, and after washing and drying is extracted with benzene until all the free alkaloid has been dissolved out. The residue consists of a 40% yield of the nitrite. When the reaction is carried out in presence of benzene the oil which separates quickly solidifies, and consists of almost pure papaverine nitrite. The substance forms an almost colourless, sandy powder which decomposes at about 140°, and, therapeutically, exhibits the tissue dilating properties of its components in an enhanced degree.

G. F. M.

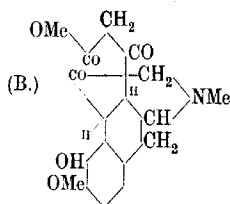
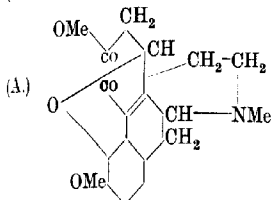
### Constitution of isoChondodendrine and Thebaine.

FRANZ FAITLS and THEODOR HECZKO (*Monatsh.*, 1923, 43, 377—385).—Ethyl chloroformate, in presence of potassium hydroxide, converts isoChondodendrine into a mixture of dicarbethoxyhydrochloroisochondodendrine, dicarbethoxyisochondodendrine, and N-carbethoxyhydrochloroisochondodendrine. Only a partial interaction occurs with respect to the phenolic group in the alkaloid, as in the case of bulbocapnine (A., 1921, i, 579). The product is optically active, giving  $[\alpha]_D -20^\circ$  in 96% alcohol. The chlorine atom present, from its reactivity, is apparently in the  $\alpha$ -position with respect to the benzene ring. On evaporating an alcoholic solution of the

above mixture, a carmine-red substance is formed, presumably as shown below :



By applying the Angeli-Rimini "nitroxyl reaction" to thebaizone, it is shown that the latter does not contain a free aldehyde-group, and therefore probably has the annexed formula (A), a certain amount of tautomeric change occurring, giving, also, (B). This result points to the correctness of the formula suggested by Faltis (A., 1917, i, 411) for thebaine.



F. E. T.

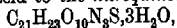
**Strychnos Alkaloids. XXXVIII. Transformations of the Four Isomeric Brucinesulphonic Acids.** HERMANN LEUCHS and HEINZ ZANDER (*Ber.*, 1923, 56, [B], 502—509).—An extension of the work of Leuchs and Geiger (A., 1909, i, 828) and Leuchs and Fricker (A., 1922, i, 677).

Brucinesulphonic acid II is converted by hot 5*N*-nitric acid into the *nitroquinone hydrate* II,  $\text{C}_{21}\text{H}_{21}\text{O}_{10}\text{N}_3\text{S}$ , orange-red, hexagonal, domatic prisms or rectangular plates which gives a *monosemicarbazone*,  $\text{C}_{22}\text{H}_{24}\text{O}_{10}\text{N}_6\text{S}$ , thin, lemon-yellow needles or prisms. It is reduced by tin and concentrated hydrochloric acid to the *aminoquinol hydrochloride*,  $\text{C}_{21}\text{H}_{23}\text{O}_7\text{N}_3\text{S}\cdot\text{HCl}$ , colourless prisms, the water added previously to give the  $\cdot\text{CO}_2\text{H}/\text{HN}\cdot$  groups being again eliminated to  $\cdot\text{CO}\cdot\text{N}\cdot$ . It is converted by sulphurous acid into the *nitroquinol hydrate* II,  $\text{C}_{21}\text{H}_{23}\text{O}_{10}\text{N}_3\text{S}\cdot 3\text{H}_2\text{O}$ , aggregates of blackish-violet prisms or needles, which, like the corresponding compound from brucinesulphonic acid I, is converted by alcoholic hydrogen chloride into a violet *diethyl* derivative containing the carbethoxyl and the quinonoid,  $\cdot\text{NO}\cdot\text{OEt}$ , groups. It is transformed by acetic anhydride and sodium acetate into a *triacetyl* compound,  $\text{C}_{27}\text{H}_{23}\text{O}_{13}\text{N}_3\text{S}$ , short needles or five-sided plates.

Brucinesulphonic acid III is transformed by 5*N*-nitric acid into the *nitroquinone hydrate* III,  $\text{C}_{21}\text{H}_{21}\text{O}_{10}\text{N}_3\text{S}$ , orange-coloured, hexagonal platelets which is reduced by sulphurous acid to the *nitroquinol hydrate* III,  $\text{C}_{21}\text{H}_{23}\text{O}_{10}\text{N}_3\text{S}\cdot 3\text{H}_2\text{O}$ , lustrous, blackish-violet prisms or leaflets.

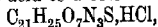
Brucinesulphonic acid, IV, and 5*N*-nitric acid at 0—10° yield the *quinone nitrite*,  $\text{C}_{21}\text{H}_{20}\text{O}_7\text{N}_2\text{S}\cdot\text{HNO}_2\cdot 5\text{H}_2\text{O}$ , red plates, whereas when the substances are heated together on the water-bath after

being diluted, the *nitroquinone hydrate*,  $C_{21}H_{21}O_{10}N_3S_2H_2O$ , orange, coloured, domatic prisms, separates. The latter substance is reduced by sulphurous acid to the *nitroquinol hydrate* IV,

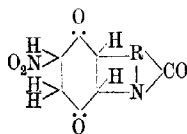


lustrous, pale reddish-violet needles or dark violet-red prisms.

The nitroquinone hydrate I is converted by saturated bromine water at  $15-20^\circ$  into the *product*,  $C_{21}H_{23}O_{11}N_3Br_2S_2 \cdot 2H_2O$ , pale yellow, oblique platelets or short prisms in which the water may be present as solvent of crystallisation; this cannot be regarded as definitely established, since the compound is so unstable that it can only be desiccated at  $20^\circ$ . A profound change appears, however, to have taken place, since sulphurous acid removes the bromine without regenerating the violet nitroquinol, in place of which a *product*,  $C_{21}H_{23}O_9N_3S$ , pale yellow, oblique, four-sided plates, is obtained in which the nitro-group is retained, since it is reduced by tin and hydrochloric acid to a colourless *amine* salt,



which evolves ammonia when boiled with potassium hydroxide solution. The absence of an oxygen atom in the new nitro-compound as compared with the nitroquinol hydrate is explained by the loss of water involved in the conversion of the groups  $-CO_2H:NH$  to  $:N-CO$ ; in this case, four atoms of hydrogen must have been added, which occurs probably as



indicated in the annexed formula, or a tautomeric form of it. One of the bromine atoms of the dibromide is certainly attached to the carbon atom united to the nitro-group, since it evolves bromonitromethane when boiled with water and gives a bromine-

free *acid*,  $C_{19}H_{22}O_9N_2S$ ; the latter contains the sulphonic acid group, thus indicating that this radicle cannot have been present in the aromatic nucleus of brucine, which suffers fission under these conditions.

The nitro-compound,  $C_{21}H_{23}O_9N_3S$ , gives with bromine a *product*,  $C_{21}H_{23}O_9N_3SBr_2$ , which differs completely from the previous bromo-derivative. It is not de-halogenated by sulphurous acid; it gives bromopicrin when boiled with water. H. W.

**Halogen Derivatives of Quinine.** SIGMUND FRÄNKEL, OTTO HERSCHMANN, and CHARLOTTE TRITT (*Ber.*, 1923, 56, [B], 433-438).—With the ultimate object of preparing derivatives of quinine in which the secondary alcoholic hydroxyl is replaced by an amino-group or the latter is present in the vinyl residue, the preparation of halogenated quinine compounds has been investigated. Quinine chloride is readily prepared by a modified method, but does not react in the desired sense with ammonia. On the other hand, quinine does not react simply with the bromides of phosphorus. Quinine chloride does not yield the bromide when heated above its melting point with potassium bromide, whereas with potassium iodide it gives a brown, amorphous substance.

Quinine is converted by phosphorus pentabromide (molecular

ratio, 3 : 7) in the presence of boiling chloroform into a resin which is partly dissolved when subsequently treated with ice-water. Addition of ammonia to the aqueous solution causes the precipitation of a colourless base, which rapidly becomes red. The precipitate does not appear to be uniform; after repeated purification, it gives analytical results approximating to those required by a dibromide. The portion which is undissolved by water contains two crystalline *tribromides*,  $C_{20}H_{22}ON_2Br_3$ , which have, respectively, m. p.  $109^\circ$  and  $[\alpha]_D^{19} + 198^\circ$  in methyl-alcoholic solution and  $235-245^\circ$  (corr. decomp.),  $[\alpha]_D^{19} + 119^\circ$  in chloroform. When quinine and phosphorus pentabromide in the molecular ratio 3 : 5 are allowed to react under similar conditions, the product is a *tribromide*, decomp.  $217^\circ$ , whereas when the substances are employed in molecular proportions a *dibromide*, m. p.  $130^\circ$ , is obtained. When quinine is treated with a molecular proportion of phosphorus tribromide, a monobromide appears to be produced, which, however, is mixed with a considerable proportion of unchanged quinine, from which it cannot be separated.

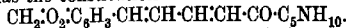
The preparation of quinine chloride,  $C_{20}H_{22}ON_2Cl$ , from quinine hydrochloride and phosphorus pentachloride is described in detail; the substance crystallises with half a molecular proportion of benzene. H. W.

**Japanese Yew Leaves. I. [Taxine].** HEISABURO KONDO and UMETARO AMANO (*J. Pharm. Soc. Japan*, 1922, 1074—1084; cf. Thorpe and Stubbs, T., 1902, 81, 874).—Taxine isolated from the leaves of yew (*Taxus baccata*) produced in the Province of Hida is a white, amorphous powder of bitter taste, m. p.  $105-111^\circ$  after sintering at  $82^\circ$ . Analysis confirmed the formula  $C_{37}H_{51}O_{10}N$  previously assigned to the alkaloid; in 5 and 10% alcoholic solutions it has  $[\alpha]_D^{18} + 32^\circ 20'$  and  $+35^\circ$ , respectively. Two chloroaurates were obtained (cf. *loc. cit.*), one, m. p.  $90-105^\circ$  (decomp.), soluble into hot dilute hydrochloric acid, and the other,  $C_{37}H_{51}O_{10}N \cdot HAuCl_4$ , m. p.  $110^\circ$  (decomp.), insoluble in hot dilute hydrochloric acid. When heated with 5% sulphuric acid, the alkaloid is partly decomposed, a compound reducing Fehling's solution being produced, which, however, has not the characteristics of sugar. Emulsin is without action on the alkaloid. When heated with alcoholic potash taxine is decomposed into formic and acetic acids, an amorphous acid, m. p.  $94-95^\circ$ , and molecular weight 215, a crystalline acid (perhaps cinnamic acid), m. p.  $133^\circ$ , and a compound,  $C_{23}H_{33}O_4N$ , m. p.  $105-110^\circ$ , insoluble in dilute sulphuric acid. By bromination in glacial acetic acid, the alkaloid gave a *tetrabromide*,  $C_{37}H_{51}O_{10}NBr_4$ , a yellow, amorphous powder, whilst in dilute sulphuric acid solution, a *tribromide*,  $C_{37}H_{51}O_{10}NBr_3$  or  $C_{37}H_{51}O_{10}NBr_2 \cdot HBr$ , a light yellow, amorphous powder, is formed. K. K.

**The Relationship between Constitution and Taste of Pepper.** I. H. STAUDINGER and HERMANN SCHNEIDER (*Ber.*, 1923, 56, [B], 699—711).—The investigation was undertaken with the object of finding a suitable substitute for pepper. The taste

of the latter is due to the presence of piperine, the physiological action of which is largely influenced by the dispersivity; the required taste is only developed when it is very finely divided.

Piperine has the constitution



For the development of the pepper taste, it is essential that the piperidine should be in amide-like union with an aliphatic-aromatic acid. It is most noticeable with derivatives of  $\delta$ -phenyl- $n$ -valeric acid. The possibilities of variation of the acidic component have been fully examined whilst those connected with the basic portion will be described in a subsequent communication. It is found that the presence of the methylenedioxy-group and of double bonds is not essential to the development of pepper taste, whilst also the stereochemical configuration of the chain does not appear to exert a marked influence. On the other hand, it is necessary that the phenyl group and the four carbon atoms in the side chain should be present. Piperine may be completely replaced by a mixture of the piperidides of  $\delta$ -phenyl- $\Delta^5$ - and - $\Delta^4$ -pentenoic acids dissolved in phellandrene.

Cinnamylidenemalonic acid is conveniently prepared in 88.6% yield by the action of glacial acetic acid on a mixture of calcium malonate and cinnamaldehyde at 60–70° and subsequent protracted heating of the product at 80°, and finally at 100°. It is converted by phosphorus pentachloride in the presence of benzene into *cinnamylidenemalonyl chloride*, golden-yellow crystals, m. p. 83°, which is stable towards water, and is transformed into a piperide which has not a pronounced taste of pepper.

Cinnamaldehyde reacts with malonic acid in the presence of pyridine to give cinnamenylacrylic acid, m. p. 165°, whereas in the presence of quinoline, *allocinnamenylacrylic acid*, m. p. 138°, is produced. (*Pyridine hydrogen cinnamylidenemalonate* crystallises in colourless needles, m. p. 114–115°, decomp., and gives when heated cinnamenylacrylic acid, m. p. 165°, in about 60% yield, and an acid of lower melting point which has not been investigated. *Quinoline hydrogen cinnamylidenemalonate* has m. p. 114–115° and decomposes at about 130° yielding mainly *allocinnamenylacrylic acid*, m. p. 138°, other non-crystalline acids and very little acid, m. p. 165°.) Cinnamenylacrylic acid, m. p. 165°, is converted into the corresponding *chloride*, m. p. 47°, by the action of a solution of thionyl chloride in boiling light petroleum and thence into the *piperidide*, m. p. 91–92°, which after being ground with flour during ten days has a very pronounced taste of pepper. *allo-Cinnamenylacrylic acid* is converted by similar methods into a non-crystalline *chloride* and *piperidide*; the taste of the latter appears to be indistinguishable from that of its isomeride.

Cinnamylidenemalonic acid is reduced by sodium amalgam in faintly alkaline solution to dihydrocinnamylidenemalonic acid, which is decomposed in boiling aqueous solution into  $\delta$ -phenyl- $\Delta^5$ -pentenoic acid; the corresponding *chloride*, a colourless liquid, b. p. 139–140°/12 mm., 98–100°/0.2 mm., prepared by the action of thionyl chloride in the presence of benzene or light petroleum;

the *anilide*, m. p. 80—82°; the *ethyl ester*, b. p. 154—156°/11 mm., and the *piperidide*, a viscous liquid, b. p. 163—165°/0.2 mm., are described. If, on the other hand, dihydrocinnamylidenemalonic acid is decomposed in the presence of boiling pyridine, it gives mainly  $\delta$ -phenyl- $\Delta^2$ -pentenoic acid; the corresponding *chloride*, a colourless liquid, b. p. 149—150°/15 mm., *anilide*, m. p. 115°; *ethyl ester*, a colourless liquid, b. p. 156—159°/13 mm., and *piperidide*, a viscous liquid, b. p. 164—169°/0.2 mm., are described.

[With E. PFISTER.]— $\delta$ -Phenyl- $\Delta^2$ -pentenoic acid is converted by thionyl chloride in the presence of boiling light petroleum into the corresponding *chloride*, b. p. 100—105°/0.15 mm., and thence into the *piperidide*, a pale yellow, viscous liquid, b. p. 165—167°/0.2 mm., which has a very marked taste of pepper.

[With H. BRÜTSCH.]— $\alpha$ -Phenylcinnamylacrylyl chloride, m. p. 87—89°, is prepared by the protracted action of a solution of thionyl chloride in boiling benzene on the corresponding acid and is converted into the *piperidide*, m. p. 135°, which has not a sharp taste.

[With A. GIUGLIEMETTI.]—Sorbyl chloride, b. p. 69—71°/12 mm., prepared from the acid and thionyl chloride in the presence of boiling benzene, gives the corresponding *piperidide*, m. p. 83—84°.

H. W.

**The Relationship between Constitution and Taste of Pepper. II. The Piperidides of Fatty-aromatic Acids.** H. STAUDINGER and FRITZ MÜLLER (*Ber.*, 1923, 56, [B], 711—715; cf. preceding abstract).—The taste of the piperidides of fatty-aromatic acids is influenced in an oscillating manner by the number of methylene groups in the chain, compounds with 2, 4, or 6 such groups having a sharper taste than those with 1, 3, or 5 groups. The taste of pepper is particularly pronounced in the case of the piperidide of  $\delta$ -phenyl-*n*-valeric acid. With unsaturated acids, the connexion between taste and constitution is not so marked, but the amount of material available scarcely permits exact conclusions to be drawn.

Phenylacetopiperidide, prepared from phenylacetyl chloride and piperidine, is an almost colourless liquid, b. p. 138—139°/0.4 mm.  $\beta$ -Phenylpropionylpiperidide, prepared similarly, has b. p. 147—150°/0.14 mm.  $\gamma$ -Phenylbutyric acid, m. p. 46—47°, is conveniently prepared in 94% yield of heating  $\beta$ -benzoylpropionic acid with hydrazine hydrate and sodium ethoxide at 180°; the corresponding *piperidide* has b. p. about 155°/0.25 mm.  $\delta$ -Phenylvaleric acid is readily prepared in large quantity by reducing cinnamylidenemalonic acid with sodium amalgam to dihydrocinnamylidenemalonic acid, and converting the latter by loss of carbon dioxide into  $\delta$ -phenyl- $\Delta^2$ -pentenoic acid, which is hydrogenated in alcoholic solution in the presence of platinum or in neutral aqueous solution in the presence of palladium; the acid has m. p. 57°. The corresponding *piperidide* is a liquid, b. p. about 164°/0.24 mm.  $\epsilon$ -Phenylhexoic acid is converted by thionyl chloride and benzene into the corresponding *chloride*, b. p. 151—

152°/11 mm., and thence into the *piperidide*, a pale yellow liquid, b. p. about 177°/0.05 mm.  $\zeta$ -Phenylheptioic acid, a colourless liquid which solidifies when strongly cooled, is conveniently prepared from  $\epsilon$ -phenylamyl bromide by the malonic ester synthesis; it yields successively the *chloride*, b. p. 166–168°/11 mm., and the *piperidide*, a pale yellow liquid, b. p. 184–188°/0.01 mm.

[With H. HALTEN.]—The *piperidide* of  $\gamma$ -phenyl- $\Delta^2$ -isocrotonic acid crystallises in colourless needles, m. p. 64–65°. H. W.

**The Formation of Quaternary Ammonium Salts.** I. EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and ERNEST PERCY DRISCOLL (T., 1923, 123, 503–518).

**The Dissociation of N-Pentamethylene-S-triarylmethylthiourethanes [Triarylmethyl Piperidine-1-carbodithionate] with the Formation of Triarylmethyls.** F. F. BLICKE (J. Amer. Chem. Soc., 1923, 45, 544–549).—Triphenylmethyl piperidine-1-carbodithionate and some of its homologues were prepared by the interaction of piperidine piperidine-1-carbodithionate and the corresponding triarylchloromethane. These esters in solution, at the ordinary temperature, dissociate with the formation of free triarylmethyl radicles, which on exposure to air are converted into their insoluble peroxides. Thus *triphenylmethyl piperidinocarbodithionate*,  $C_5H_{10}N-CS_2CPh_3$ , m. p. 155–160° (decomp.), gives triphenylmethyl peroxide; the *diphenyl- $\alpha$ -naphthylmethyl* ester gives diphenyl- $\alpha$ -naphthylmethyl peroxide, and the *diphenyldiphenylmethyl* ester gives diphenyldiphenylmethyl peroxide. W. G.

**Pyrroles. IV. Pyrrolealdehydes (II) and Pyrrolenitriles.** HANS FISCHER and WERNER ZERWECK (Ber., 1923, 56, [B],

519–527).—2:3:5-Trimethylpyrrole-4-aldehyde,  $NH < \begin{matrix} CMe:CMe \\ CMe:C:CHO \end{matrix}$  colourless crystals, m. p. 143.5°, is prepared in 66.6% yield by the action of hydrogen chloride on a solution of 2:3:5-trimethylpyrrole and anhydrous hydrogen cyanide in chloroform and decomposition of the product of the reaction with water; it is remarkable that the chloroform cannot be replaced by ether as solvent. The following derivatives are described: *phenylhydrazone*, coarse, brown crystals, m. p. 138°; *oxime*, colourless needles, m. p. 164°; *semicarbazone*, m. p. 198°; *aldazine*, m. p. 273° after previous darkening. Attempts to convert the aldehyde into 2:3:5-trimethylpyrrole-4-propionic acid were unsuccessful. The aldehyde is converted by hippuric acid and sodium acetate into the *azlactone*,  $C_{17}H_{18}O_2N_2$ , orange or reddish-brown needles, m. p. 198°, which is transformed by sodium hydroxide into 2:3:5-trimethylpyrrole-4-benzoylaminoacrylic acid,  $C_{17}H_{18}O_3N_2$ , m. p. 178° (decomp.), which could not, however, be reduced. Similarly, the propionic acid derivative could not be obtained through the product (m. p. 286°) of the condensation of the aldehyde with rhodamine.

2:4-Dimethylpyrrole-5-aldehyde is prepared in 92% yield by

the action of hydrogen chloride and hydrogen cyanide on 2:4-dimethylpyrrole in the presence of chloroform, whereas the yield is only moderate if ether is used as solvent (cf. Fischer and Zerweck, A., 1922, i, 758).

4-Cyanoacetyl-2:3:5-trimethylpyrrole is converted by alcoholic sodium hydroxide solution at 160° into 4-acetyl-2:3:5-trimethylpyrrole, m. p. 207°.

A series of pyrrolenitriles, in which the cyano-group is attached to a ring carbon atom, has been prepared from the aldehydes through the oximes; reaction proceeds so smoothly that the method is of preparative value. Thus, ethyl 4-aldehyde-2:5-dimethylpyrrole-3-carboxylate is converted into the *oxime*, colourless crystals, m. p. 223° (decomp.), which is transformed by acetic anhydride and anhydrous sodium acetate into ethyl 4-cyano-2:5-

dimethylpyrrole-3-carboxylate,  $\text{NH} < \begin{matrix} \text{CMe}=\text{C}\cdot\text{CN} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et}' \end{matrix}$  colourless, lustrous needles, m. p. 152°. Ethyl 5-cyano-2:4-dimethylpyrrole-3-carboxylate forms colourless crystals, m. p. 159°; 4-cyano-2:3:5-trimethylpyrrole has m. p. 140°.

Attempts to prepare 2:3:4:5-tetramethylpyrrole by the action of hydrogen iodide and glacial acetic acid on 2:3:5-trimethylpyrrole-4-aldehyde were unsuccessful, owing to loss of the formyl groups. (Ethyl 5-aldehyde-2:4-dimethylpyrrole-3-carboxylate is converted under similar conditions into 2:4-dimethylpyrrole.) The tetramethyl compound is, however, obtained by the action of alcoholic sodium ethoxide solution at 150–160° on the semicarbazone of 2:3:5-trimethylpyrrole-4-aldehyde; it is isolated as the *picrate*, coarse, yellow crystals, m. p. 130°. Similarly, ethyl 4-aldehyde-2:5-dimethylpyrrole-3-carboxylate semicarbazone, colourless crystals, decomp. 257° after softening at about 244°, yields 2:3:5-trimethylpyrrole.

The stability of the formyl group in substituted pyrroles towards alkali hydroxide is remarkable. Thus, 2:3:5-trimethylpyrrole-4-aldehyde is unchanged by boiling, aqueous sodium hydroxide solution (20%); ethyl 5-aldehyde-2:4-dimethylpyrrole-3-carboxylate is converted into 5-aldehyde-2:4-dimethylpyrrole-3-carboxylic acid, m. p. 283–284° (decomp.), and ethyl 4-aldehyde-2:5-dimethylpyrrole-3-carboxylate gives 4-aldehyde-2:5-dimethylpyrrole-3-carboxylic acid, m. p. 248° (decomp.).

2:4-Dimethylpyrrole-5-aldehyde is transformed by concentrated hydrochloric acid into *di*-2:4-dimethylpyrrolmethene, m. p. 18°. *Di*-3-carbethoxy-2:4-dimethylpyrrolmethene hydrochloride is most conveniently prepared by heating ethyl 2:4-dimethylpyrrole-3-carboxylate dissolved in concentrated hydrochloric acid with an excess of formic acid; the corresponding base crystallises in long, dark red needles, m. p. 190°.

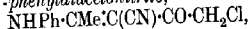
4-Chloroacetyl-2:3:5-trimethylpyrrole is converted by an alcoholic solution of dimethylamine into 4-dimethylaminoacetyl-2:3:5-trimethylpyrrole hydrochloride, colourless crystals, m. p. 48°; the corresponding base has m. p. 130°. 4-Phthalimidoacetyl-2:3:5-trimethylpyrrole has m. p. 227°.

H. W.

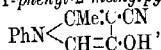
**Hydroxypyrrole Derivatives. III.** ERICH BENARY and WILHELM LAU (*Ber.*, 1923, 56, [B], 591—597; cf. Benary and Silbermann, A., 1913, i, 651).—An account of partly completed work induced by the recent publications of Küster (A., 1922, i, 857), Küster and Maag (this vol., i, 242), and Fischer and Hermann (A., 1922, i, 1054).

*C-Chloroacetyldiacetonitrile*,  $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , colourless needles, m. p.  $155^\circ$ , is prepared by the action of chloroacetyl chloride on diacetonitrile in the presence of pyridine. The constitution of the compound follows from the observation that it is converted by potassium hydrogen sulphide into the corresponding *sulphide*,  $[\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2]_2\text{S}$ , colourless, matted needles, m. p.  $178\text{--}179^\circ$ , in which the amino-group is readily replaced by hydroxyl by means of *N*-sodium hydroxide solution with production of the *dienol*,  $[\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2]_2\text{S}$ , colourless needles, m. p.  $130^\circ$ . The conversion of the chloroacetyl compound into the corresponding hydroxypyrrole has not yet been accomplished definitely. In general, the preparation of the latter compounds can frequently be satisfactorily effected only under very definite experimental conditions, which must be established for each particular case.

*C-Chloroacetyl-N-phenyldiacetonitrile*,



colourless leaflets, m. p.  $103\text{--}104^\circ$ , is prepared from *N*-phenyldiacetonitrile and chloroacetyl chloride in the presence of pyridine and ether, and is transformed by potassium hydrogen sulphide into the *sulphide*,  $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_4\text{S}$ , colourless needles, m. p.  $170\text{--}172^\circ$ . It is transformed by potassium hydroxide in the presence of methyl alcohol into 4-hydroxy-1-phenyl-2-methylpyrrole-3-nitrile,



colourless needles, m. p.  $167^\circ$ , which is converted by nitrous acid into 5-oximino-4-keto-1-phenyl-2-methylpyrroline-3-nitrile, orange-yellow needles, decomp.  $178^\circ$  after darkening at about  $160^\circ$ , and by sodium nitrite and glacial acetic acid into 5-nitroimino-4-keto-

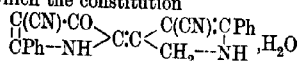
1-phenyl-2-methylpyrroline-3-nitrile,  $\text{PhN} \begin{array}{c} \text{CMe} \\ \diagdown \quad \diagup \\ \text{C}(\text{N}\cdot\text{NO}_2)\cdot\text{CO} \end{array}$ , an

orange-coloured precipitate, decomp.  $225^\circ$ . The latter substance is transformed by sodium hydroxide solution (5%) into the substance,  $\text{NPh}\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{NH}_2)\cdot\text{C}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}_2$ , pale-yellow, four-sided plates, decomp.  $240\text{--}241^\circ$  after becoming altered at  $237^\circ$ , which, with phenylhydrazine in the presence of acetic acid (50%), yields the compound,

$\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}\cdot\text{NH}_2)\cdot\text{CMe}\cdot\text{NPh}$ , brownish-yellow needles or four-sided prisms, decomp.  $225^\circ$  after gradual darkening and softening above  $205^\circ$ .

*C-Chloroacetylbenzoacetodinitrile*,  $\text{NH}_2\cdot\text{CPh}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , long, colourless needles, m. p.  $116^\circ$ , is converted in the usual manner into the corresponding *sulphide*,  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_4\text{S}$ , colourless needles, m. p.  $195\text{--}198^\circ$ . Attempts to transform it into the corresponding

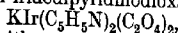
pyrrole resulted in the production of a reddish-violet dye, decomp. about 250°, for which the constitution



is suggested.

H. W.

**Potassium Iridodipyridinodioxalates.** MARCEL DELÉPINE (*Compt. rend.*, 1923, 176, 445—447).—When *r-cis*-potassium iridodichlorodioxalate is heated with pyridine at 130° for four hours, a crystalline potassium iridodipyridinodioxalate,



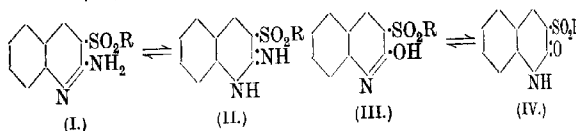
is obtained together with an amorphous product, which has the same composition as the crystalline product. The crystalline salt when treated with aqua regia is converted into a dipyridino-iridium tetrachloride, which with ammonia gives the same special complexes as the chloride from the red salts. Similarly, if the dioxalate is treated with hydrochloric acid, it gives a series of compounds among which is an iridodipyridino-tetrachloride of iridodichlorodiaquodipyridine. This salt reacts with alkalis to give a red iridodipyridino-tetrachloride, and a hydroxy-compound which is an anhydride of the theoretical hydroxide of the salt,  $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})(\text{OH})\text{Cl}_2$ . The other products formed in the decomposition by hydrochloric acid are the aquodipyridinoiridium chloro-oxalate,  $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})\text{Cl}(\text{C}_2\text{O}_4)$ , a neutral substance insoluble in water but soluble in alkalis, and iridodichlorodiaquodipyridine chloride,  $\text{Cl}[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ , and traces of potassium pyridinoiridium pentachloride. The iridodipyridinodioxalate is therefore, apparently a *trans*-dipyridino-compound formed by intramolecular transpositions. The amorphous compounds obtained along with it are the *cis*-compounds and give orange-coloured salts under the influence of hydrochloric acid. W. G.

**Amino-alcohols, Ketones, and other Derivatives of the Quinoline Series.** K. MIESCHER (U.S. Pat. 1434306).—*Ethyl 2-phenylquinoline-4-acetate*, yellow prisms, m. p. 52—54°, is obtained from the reaction products of ethyl 2-phenylquinoline-4-carboxylate, sodium ethoxide, and ethyl acetate heated in toluene for twenty-four hours. It forms a sparingly soluble, bright green copper salt, and intensely yellow salts with hydrochloric and sulphuric acids. *2-Phenyl-4-quinolyl methyl ketone*, yellow crystals, m. p. 73°, is formed by heating ethyl 2-phenylquinoline-4-acetate with eight times its weight of 25% sulphuric acid and treating the reaction mass with sodium carbonate and ether, or from a solution of 4-cyano-2-phenylquinoline in benzene treated drop by drop, with cooling, with a solution of magnesium methyl iodide in ethyl ether (*hydrobromide*, yellow, m. p. 240°). Bromination of the ketone in concentrated hydrobromic acid or an organic solvent yields the *hydrobromide*, m. p. about 225° (decomp.), of *2-phenyl-4-quinolyl bromomethyl ketone*, bright yellow crystals, m. p. 91°. The latter hydrobromide reacts in benzene cooled with ice with dimethylamine, subsequent treatment with alcoholic hydrogen

chloride giving 2-phenyl-4-quinolyl dimethylaminoethyl ketone mono-hydrochloride, yellow crystals, m. p. 208° (decomp.) (hydrobromide, m. p. about 206°). 2-Phenyl-4-quinolyl diethylaminoethyl ketone monohydrochloride forms bright yellow needles, m. p. about 164° (decomp.); 2-phenylquinolyl 4-piperidylethyl ketone monohydrochloride has m. p. 235° [monohydrobromide, m. p. about 241° (decomp.)]. Amino-alcohols containing a primary amino-group can be prepared by reducing the corresponding oximinoketones, *N*-substituted amino-alcohols being similarly obtained from amino-ketones. 2-Phenyl-4-quinolylaminoethanol dihydrochloride forms yellow crystals, m. p. 145°. 2-Phenyl-4-quinolyl dimethylaminoethanol dihydrochloride has m. p. about 175° (decomp.), and the corresponding diethylamino compound, m. p. about 185°. 2-Phenyl-4-quinolylpiperidylethanol has m. p. about 54° (monohydrochloride, m. p. about 162°; dihydrochloride, m. p. about 199°).

CHEMICAL ABSTRACTS.

**Syntheses of 2- and 3-Substituted Quinolines.** JULIUS TRÖGER and PAUL KÖPPEN-KASTROP (*J. pr. Chem.*, 1922, [ii], 104, 335—367).—The condensation of *o*-aminobenzaldehyde with an arylsulphonylacetonitrile, using pyridine as catalyst, gives, instead of the expected product  $\text{RSO}_2\text{C}(\text{CN})\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , a quinoline derivative (I), in the formation of which both hydrogen atoms of the amino-group must have migrated to the nitrogen of the cyano-group (cf. Pshorr, A., 1898, i, 491); the same compound is produced by the re-



duction in alcoholic hydrogen chloride solution with stannous chloride of the condensation product,  $\text{RSO}_2\text{C}(\text{CN})\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , of *o*-nitrobenzaldehyde and an arylsulphonylacetonitrile. Nitrous acid converts these aminoquinolines into carbostyryl derivatives (III), the structure of which is firmly established by their synthesis from *o*-aminobenzaldehyde and (a) the arylsulphonylacetic acid, (b) its ester, or (c) its amide, with elimination of (a) water, (b) alcohol, or (c) ammonia, respectively. Although these carbostyryl derivatives are insoluble in aqueous alkali, they form sodio-derivatives in the absence of water, which lead to 3-arylsulphonyl-2-alkoxyquinolines when treated with alkyl halides under pressure; moreover, the hydroxyl may be replaced by chlorine by means of phosphorus pentachloride. Hence these carbostyryls are best represented as tautomeric in the sense  $\text{(III)} \rightleftharpoons \text{(IV)}$ . The properties of the amino-compounds are less easy to explain. They are insoluble in concentrated hydrochloric acid, and cannot be diazotised even at a high temperature and pressure, neither do they react with methyl iodide, although with this reagent the  $\beta$ -arylsulphonylmethylquinolines (Tröger and Menzel, A., 1922, i, 269) form crystalline derivatives. It is equally surprising that the salts and double

salts are much more readily dissociated than those of the corresponding 2-methyl derivatives. This is even difficult to understand if a tautomeric form (II) is assumed, since this should give at least a mono-alkyl derivative. Nitrous acid would then convert (II) into (IV). The formation of the  $\alpha$ -chloro-compound is certainly more easily explained on formula (III); nevertheless, the action of a large excess of phosphorus halide leads to a dichloro-derivative, possibly derived from the keto-form (IV).

The 2-chlorine atom is readily replaceable by ethoxyl (using sodium ethoxide); also by the  $\cdot\text{SH}$  group (by means of alcoholic potassium hydrosulphide) giving a thiocarbostyryl, which is soluble in aqueous alkali and more readily alkylated than the carbostyryl itself. Replacement by the group  $\text{R}\cdot\text{SO}_2\cdot$ , by the action of a salt of an arylsulphinic acid, proceeds only slowly, whilst the replacement by the group  $\text{Na}\cdot\text{SO}_3\cdot$  (by means of sodium sulphite, cf. Besthorn and Geisselbrecht, A., 1920, i, 563) has not been accomplished.

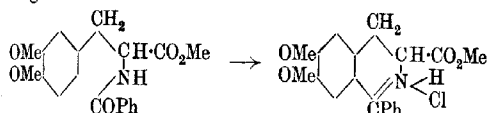
The above reactions have been investigated when R is  $\text{C}_6\text{H}_5\cdot$ ,  $\text{H}_3\cdot\text{C}_6\text{H}_4\cdot(p)$ , and  $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot(p)$ .

Equimolecular quantities of *o*-nitrobenzaldehyde and benzenesulphonylacetonitrile give, when treated in concentrated alcoholic solution with a little pyridine,  $\beta$ -*o*-nitro- $\alpha$ -benzenesulphonylcinnamionitrile, long, slender, white needles, m. p.  $149^\circ$ , which on reduction by means of stannous chloride and hydrochloric acid in alcoholic solution is converted into 2-amino-3-benzenesulphonylquinoline, long, white needles, m. p.  $206^\circ$ , which is also produced by heating *o*-aminobenzaldehyde and benzenesulphonylacetonitrile in alcoholic solution with a little aqueous sodium hydroxide. The hydrochloride, needles, decomp.  $100^\circ$ , the nitrate, needles, decomp.  $70^\circ$ , the hydrogen sulphate, yellow needles, decomp.  $105^\circ$ , the hydrogen oxalate, the perchlorate, the chloroplatinate,  $(\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$ , reddish-yellow needles, and the chloroaurate,  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2\text{S}\cdot\text{HAuCl}_4$ , golden needles, m. p.  $200^\circ$ , are described. The amino-compound, which cannot be alkylated, reacts in somewhat dilute acetic acid solution with sodium nitrite to give 3-benzenesulphonylcarbostyryl, long, rod-like prisms, m. p.  $312^\circ$ , which is also produced when *o*-aminobenzaldehyde is heated under pressure with either ethyl benzenesulphonylacetate or benzenesulphonylacetonitrile. 3-Benzenesulphonyl-2-thoxyquinoline, small, pale yellow prisms, m. p.  $190^\circ$ , is produced by heating the sodium salt of the carbostyryl in alcoholic suspension with methyl iodide under pressure, more readily by the action of sodium ethoxide at  $100^\circ$  on 2-chloro-3-benzenesulphonylquinoline, broad, rod-like crystals, m. p.  $150^\circ$ , which is produced by heating the  $\alpha$ -hydroxy-compound at  $160^\circ$  with phosphorus pentachloride and a few drops of phosphoryl chloride. When this chloro-derivative is heated at  $100^\circ$  with sodium benzenesulphinate, 2 : 3-dibenzesulphonylquinoline, small, yellowish-white needles, m. p.  $204^\circ$ , is formed, the 2-substituent of which is replaced by hydroxyl by fusion with alkali hydroxide; with alcoholic potassium hydrosulphide at  $100^\circ$ , the product is 3-benzenesulphonylthiocarbostyryl, long slender, yellow needles, m. p.  $241^\circ$ , which, when shaken with

methyl sulphate and dilute aqueous sodium hydroxide, gives a *s*-methyl derivative, long, yellow needles, m. p. 175°. The condensation of *o*-nitrobenzaldehyde with *p*-toluenesulphonylacetonitrile by means of pyridine in alcoholic solution leads to *o*-nitro- $\alpha$ -*p*-toluenesulphonylcinnamonnitrile, long, yellowish-white needles, m. p. 152°, which on reduction gives 2-amino-3-*p*-toluenesulphonylquinoline, sulphur-yellow, rod-like crystals, m. p. 214°, which is also produced by the condensation of *o*-aminobenzaldehyde with *p*-toluenesulphonylacetonitrile; the hydrochloride, slender needles, decomp. 100°, the nitrate, slender needles, decomp. 70°, the hydrogen sulphate, decomp. 100°, the hydrogen oxalate, the chloroplatinate (+H<sub>2</sub>O), reddish-yellow prisms, and the chloroaurate, slender, golden-yellow needles, m. p. 207°, are described. 3-*p*-Toluenesulphonylcarbostyryl, small, yellow prisms, m. p. 300°, is formed from the amino-compound by the action of nitrous acid, and also by heating *o*-aminobenzaldehyde at 160–170° with ethyl *p*-toluenesulphonylacetate, *p*-toluenesulphonylacetic acid, or *p*-toluenesulphonylacetamide; it forms a yellowish-white sodium salt when treated with alcoholic sodium ethoxide. The *O*-ethyl ether, m. p. 207–207.5°, can only be prepared by the action of alcoholic sodium ethoxide at 100° on 2-chloro-3-*p*-toluenesulphonylquinoline, m. p. 178–179°, which is best prepared by the action of a slight excess of phosphorus pentachloride and a little phosphoryl chloride on the carbostyryl. By the use of a large excess of these reagents, a material, m. p. 132°, probably 2:2-dichloro-3-*p*-toluenesulphonylquinoline, has been isolated (see above), and also a product, m. p. 122–124°, containing 2% more chlorine than the dichloro-compound.  $\alpha$ -*p*-Chlorobenzenesulphonyl-*o*-nitrocinnamonnitrile, long, white needles, m. p. 156°, is formed from *o*-nitrobenzaldehyde and *p*-chlorobenzenesulphonylacetonitrile, and gives on reduction 2-amino-3-*p*-chlorobenzenesulphonylquinoline, yellow prisms, m. p. 205°, which is also produced by the condensation of *o*-aminobenzaldehyde with *p*-chlorobenzenesulphonylacetonitrile; the hydrochloride, fine needles, the nitrate, slender, white needles, the hydrogen sulphate, fine, white needles, and the hydrogen oxalate, white needles, have been prepared. This amino-compound gives, with nitrous acid, 3-*p*-chlorobenzenesulphonylcarbostyryl, yellow prisms (+16% water or acetic acid), m. p. 287°, which is also formed by the condensation at 170° of *o*-aminobenzaldehyde with ethyl *p*-chlorobenzenesulphonylacetate, and gives with sodium ethoxide a yellow, amorphous sodium salt. The *O*-ethyl ether, slender, white needles, m. p. 173°, is formed by the action of alcoholic sodium ethoxide under pressure on 2-chloro-3-*p*-chlorobenzenesulphonylquinoline, slender, ivory-coloured needles, m. p. 170°, which is produced by the action of phosphorus pentachloride and a little phosphoryl chloride on the carbostyryl. This 2-chloro-derivative, when heated at 100° in alcoholic solution with potassium hydrogen sulphide, gives impure 3-*p*-chlorobenzenesulphonylthiocarbostyryl, a yellow, amorphous substance, which with dilute aqueous sodium hydroxide and methyl sulphate gives the *S*-methyl ether, long, slender, yellow needles, m. p. 194°.

W. S. N.

**Preparation of Derivatives of Dihydroisoquinoline.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 191233).—Therapeutically active derivatives of dihydroisoquinoline are obtained by hydrogenising  $\alpha$ -acylaminocinnamic esters or their nuclear substitution derivatives, and converting the dihydrocinnamic acid derivatives thus produced into derivatives of dihydroisoquinoline-3-carboxylic acid by suitable condensing agents such as phosphoryl chloride. The parent materials are obtained by heating equimolecular proportions of an aromatic aldehyde, an acylated glycine, and sodium acetate with 3 mols. of acetic anhydride, and esterifying the product, and details are given of the conversion of the following substances into isoquinoline derivatives. Methyl veratralhippurate (methyl  $\alpha$ -benzamido-3:4-dimethoxycinnamate) is hydrogenised by means of a nickel catalyst at 55° to methyl  $\alpha$ -benzamido- $\beta$ -3:4-dimethoxyphenylpropionate, fleecy needles, m. p. 104–105°, which when heated with an equal weight of phosphoryl chloride is converted into methyl 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylate, m. p. 122·5°, according to the following scheme :



The hydrochloride and hydrobromide form yellow crystals easily soluble in water, and in common with other 6:7-dihydroxy-derivatives they have the same therapeutic action as hydrastinine, but are less poisonous. With the free ester methyl iodide gives a *N*-methiodide which is sparingly soluble in water. Piperonylidenehippuric acid is in a similar way converted through  $\alpha$ -benzamido- $\beta$ -piperonylpropionic acid into methyl 6:7-methylenedioxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylate, small, colourless needles, m. p. 140·5°, which gives a hydrochloride, and a methiodide similar to those above described. Methyl  $\alpha$ -piperonylamino-3:4-methylenedioxy-cinnamate, m. p. 156–157°, yields on hydrogenation methyl  $\alpha$ -piperonylamino-3:4-methylenedioxyphenylpropionate, lustrous needles, m. p. 139–140°, which on condensation with phosphoryl chloride gives methyl 1-piperonyl-6:7-methylenedioxy-3:4-dihydroisoquinoline-3-carboxylate, m. p. 140–141°. The hydrochloride dissociates partly when dissolved in water. Methyl  $\alpha$ -cinnamoylamido-3:4-methylenedioxy-cinnamate, m. p. 192°, is in like manner converted into methyl  $\alpha$ -[ $\beta$ -phenylpropionylamido]-3:4-methylenedioxy-phenylpropionate, m. p. 127°, and then into methyl 6:7-methylenedioxy-1-phenylethyl-3:4-dihydroisoquinoline-3-carboxylate, thick prisms, m. p. 111°. The hydrochloride gives a bluish-green fluorescence in aqueous solution, and the methochloride is readily soluble in water, but less strongly fluorescent.

G. F. M.

**Synthesis of Asymmetric Homotetrahydroisoquinoline.** JULIUS VON BRAUN and FRIEDRICH ZOBEL (Ber., 1923, 56, [B], 690–696).—Previous attempts to synthesise homotetrahydroiso-

quinoline,  $C_6H_4 \begin{smallmatrix} \text{[CH}_2\text{]}_3 \\ \text{CH}_2 \end{smallmatrix} > NH$ , starting from *o*- $\gamma$ -phenoxypropylbenzonitrile, have been unsuccessful, since the initial step, namely the reduction of the cyano- to the amino-methylene group could not be effected by nascent hydrogen. Since, however, the author's experience has shown that catalytic hydrogenation is frequently more effective than treatment with nascent hydrogen, the study has been resumed. A preliminary series of experiments shows that the change can be effected under sufficiently great pressure in the presence of nickel compounds in the cases of simpler and less costly compounds. The desired synthesis is finally affected on the lines of the scheme:  $CN \cdot C_6H_4 \cdot [CH_2]_3 \cdot OPh \rightarrow NH_2 \cdot CH_2 \cdot C_6H_4 \cdot [CH_2]_3 \cdot OPh \rightarrow NH_2 \cdot CH_2 \cdot C_6H_4 \cdot [CH_2]_3 \cdot Cl \rightarrow C_6H_4 \begin{smallmatrix} \text{[CH}_2\text{]}_3 \\ \text{CH}_2 \end{smallmatrix} > NH$ . The product

appears to contain a seven-membered ring, but the authors promise an exact proof of its constitution later.

[With (Frl.) A. NELKEN.]—*o*-Methoxy-*o*-toluonitrile, a colourless liquid, b. p.  $114^\circ/14$  mm., is converted by hydrogenation at  $100^\circ$  in the presence of tetra- or deca-hydronaphthalene into a mixture of *o*-methoxymethylbenzylamine,  $OMe \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH_2$ , a mobile liquid, b. p.  $127-128^\circ/13$  mm. (hydrochloride, m. p.  $113^\circ$ ; picrate, m. p.  $164^\circ$ ; benzoyl derivative, m. p.  $71^\circ$ ), and *di*-*o*-methoxymethylbenzylamine,  $[OMe \cdot CH_2 \cdot C_6H_4 \cdot CH_2]_2 \cdot NH$ , an almost colourless, viscous liquid, b. p.  $200-205^\circ/13$  mm. (the hydrochloride and nitroso-derivative are non-crystalline; the picrate has m. p.  $156^\circ$ ).

[With G. BLESSING.]—*o*-Phenoxy-*o*-toluonitrile, m. p.  $65^\circ$ , is transformed into a mixture of *di*-*o*-phoxymethylbenzylamine, m. p.  $53^\circ$ , which yields a very sparingly soluble hydrochloride, m. p.  $158^\circ$ , and *o*-phoxymethylbenzylamine b. p.  $195-200^\circ/13$  mm., m. p.  $26-27^\circ$  (hydrochloride, m. p.  $200^\circ$ ; picrate, m. p.  $190^\circ$ ).

*o*-Methoxy-*o*-toluonitrile, b. p.  $125-127^\circ/12$  mm., yields *p*-methoxymethylbenzylamine, a colourless, mobile liquid, b. p.  $125-130^\circ/12$  mm. (hydrochloride, needles, m. p.  $205^\circ$ ; picrate, m. p.  $179^\circ$ ; acetyl derivative, colourless crystals, m. p.  $86-87^\circ$ ; phenylthiocarbamide compound, m. p.  $102-103^\circ$ ), *di*-*p*-methoxymethylbenzylamine, a colourless, rather viscous liquid, b. p.  $195-200^\circ/1$  mm. (hydrochloride, m. p.  $215^\circ$ ; a non-crystalline picrate; nitroso-derivative, m. p.  $120^\circ$ ), and apparently a small quantity of tri-*p*-methoxymethylbenzylamine.

*o*- $\gamma$ -Phenoxypropylbenzonitrile is readily hydrogenated in the presence of decahydronaphthalene at  $115^\circ$ , although the action does not proceed quite to completion. The products of the change are *o*- $\gamma$ -phenoxypropylbenzylamine (about 30%) and *di*-*o*- $\gamma$ -phenoxypropylbenzylamine, which could not be distilled without undergoing decomposition, and for the present has not been investigated further. The primary base crystallises in colourless needles, m. p.  $55^\circ$ , b. p.  $230^\circ/18$  mm.; it yields a hydrochloride, m. p.  $154^\circ$ , and a picrate, pale yellow, lustrous needles, m. p.  $171^\circ$ . It is converted by concentrated hydrochloric acid at  $130^\circ$  (the experimental conditions must be exactly observed) into *o*- $\gamma$ -chloropropylbenzylamine,

a colourless, somewhat unstable liquid, which is characterised as the *hydrochloride*, m. p.  $172^{\circ}$ , and the *picrate*, coarse needles, m. p.  $175^{\circ}$ , after slight previous softening. An aqueous solution of the hydrochloride is converted by an excess of warm dilute alkali hydroxide solution into *as.-homotetrahydroisoquinoline*, which is volatile with steam. It is a colourless liquid with an odour of tetrahydroisoquinoline, b. p.  $120^{\circ}/17$  mm. It could not be caused to solidify. On exposure to air it becomes transformed into the carbonate. It yields a solid, very hygroscopic *hydrochloride*, a *chloroplatinate*, a crystalline powder, m. p.  $192^{\circ}$ , and a *nitro-derivative*, m. p.  $73-74^{\circ}$ . When treated with methyl iodide and alkali hydroxide, it gives the quaternary *iodide*,  $C_{12}H_{18}NI$ , m. p.  $182^{\circ}$ .  
H. W.

**Derivatives of Tetrahydrocarbazole. II.** WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT (T., 1923, 123, 676-695).

**The Action of Nitrobenzene on the Sodium and Potassium Derivatives of Carbazole.** GUILLAUME DE MONTMOLLIN and MARCEL DE MONTMOLLIN (*Helv. Chim. Acta*, 1923, 6, 94-101).—The sodium and potassium derivatives of carbazole dissolve in nitrobenzene with a dark red colour, but no compound is formed at first. On heating for some hours at  $45-50^{\circ}$ , however, reaction takes place with formation of *9-p-nitrophenylcarbazole*, crystallising in yellow spangles with a green reflex, m. p.  $212^{\circ}$ ; *picrate*, garnet-red needles. The oxygen required for the reaction is provided by excess of nitrobenzene. That the nitrobenzene has, contrary to its usual behaviour, reacted in the para-position, is shown as follows. The nitro-compound was reduced and the product diazotised and converted by Gattermann's method into chlorophenylcarbazole, which was proved to be identical with that obtained by heating potassium carbazole with *p*-chlorobromobenzene. Further, the aminophenylcarbazole gave with phthalic anhydride a phthalimide isomeric but not identical with that obtained by heating potassium carbazole with *m*-bromophthalanil.

*p*-Aminophenylcarbazole, from the nitro-compound, forms a resin; its *picrate* forms yellowish-brown needles, m. p.  $200^{\circ}$  (decomp.). *p*-Acetamidophenylcarbazole crystallises in colourless plates, m. p.  $237^{\circ}$ . *p*-Phthalimidophenylcarbazole forms colourless needles, m. p.  $210^{\circ}$ ; *m*-phthalimidophenylcarbazole, obtained in only small yield by heating potassium carbazole with *m*-bromophthalanil, forms brilliant, pale red spangles, m. p.  $216^{\circ}$ .

The diazo-compounds of *p*-aminophenylcarbazole are characterised by their stability in acids and their intense colour, orange in solution or in hydrated crystals, yellow when anhydrous. *9*-Phenylcarbazole-*p*-diazonium chloride,  $C_{12}H_8N \cdot C_6H_4 \cdot N_2Cl$ , and sulphate are soluble in a dilute acid solution at  $70^{\circ}$ , crystallising on cooling in long, silky needles; the *nitrate*, which has a remarkably slight solubility in water, forms a yellow, microcrystalline precipitate. The salts are rapidly decomposed by acetates and alkalis.

$\beta$ -Naphtholazophenylcarbazole,  $C_{12}H_8N \cdot C_6H_4 \cdot N \cdot N \cdot C_{10}H_6 \cdot OH$ , forms garnet-red needles, m. p.  $230^\circ$ ; 9-p-Chlorophenylcarbazole forms small, pale yellow crystals, m. p.  $146^\circ$ ; 9-p-cyanophenylcarbazole, obtained by acting on the diazonium salt with cuprous cyanide, forms pale yellow crystals, m. p.  $165^\circ$ . Azophenylcarbazole,  $C_{12}H_8N \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot C_{12}H_8N$ , obtained by partial reduction of *p*-nitrophenylcarbazole with zinc in acid solution, forms orange spangles, m. p.  $277^\circ$ .

*p*-Nitrophenylcarbazole is destroyed by concentrated sulphuric acid, but when treated with a mixture of sulphuric and chloro-sulphonic acids in nitrobenzene suspension it gives a crystalline sulphonic acid, green needles. When reduced, this gives an amino-sulphonic acid which, when diazotised and coupled with naphthols, yields red dyes inclined to violet. The colour obtained with  $\beta$ -naphthol gives a particularly brilliant barium lake.

By nitrating *p*-nitrophenylcarbazole in nitrobenzene suspension a dinitrophenylcarbazole, small, yellow crystals, m. p.  $274^\circ$ , is obtained. The second nitro-group is probably in the 3-position in the carbazole nucleus. The alcoholic solution of the diaminophenylcarbazole prepared from this shows a vivid blue fluorescence; its diacetyl derivative forms a white, crystalline powder, m. p.  $274^\circ$ . Nitration of *p*-acetamidophenylcarbazole gave a *p*-acetamidophenyl-dinitrocarbazole, yellow crystals, m. p.  $234^\circ$ ; it is probably the 3:6-derivative. When hydrolysed it gives *p*-aminophenyl-dinitrocarbazole, m. p.  $320^\circ$ . 9-*m*-Nitrotolylcarbazole, obtained by the action of *m*-nitrotoluene on potassium carbazole, is a yellow substance, m. p.  $138^\circ$ . E. H. R.

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. IV. Hydroxymethylenephenylacetic Ester and Hydroxymethylenbenzylcyanide with Phenylhydroxylamine. H. RUPE and J. GRÜNHOFF (*Helv. Chim. Acta*, 1923, 6, 102—110; cf. A., 1921, i, 425; 1922, i, 448, 449).—Ethyl  $\alpha$ -hydroxymethylenephenylacetate condenses in the normal way with phenylhydroxylamine, but the direct product cannot be isolated as it at once loses alcohol, forming

the diphenylisooxazolone,  $\begin{array}{c} \text{CPh} \cdot \text{CH} \\ \text{CO} \text{---} \text{O} \end{array} > \text{NPh}$ , white needles, m. p.  $175^\circ$ .

The substance quickly turns yellow in the light; it dissolves in sulphuric acid with an intense blue colour, turned dark green by ferric chloride. The same compound is obtained from methyl  $\alpha$ -hydroxymethylenephenylacetate. In chloroform solution, the isooxazolone combines with bromine to form a dibromide, white, glistening leaflets, m. p. about  $180^\circ$ ; the compound cannot be recrystallised, as it immediately loses hydrogen bromide, forming

diphenylbromoisooxazolone,  $\begin{array}{c} \text{CPh} \cdot \text{CBr} \\ \text{CO} \text{---} \text{O} \end{array} > \text{NPh}$ , which has no definite m. p., but decomposes at  $164\text{--}166^\circ$ . When the diphenylisooxazolone is warmed with alcoholic potassium hydroxide, the ring is opened, with formation of trans- $\beta$ -phenylhydroxylaminomethylene-

*phenylacetic acid*, small, glistening, pyramidal crystals, m. p. 135°. This forms a grey, crystalline *silver* salt, and an *ethyl* ester, m. p. 75°. The fact that this ester is quite stable and cannot be converted into the isooxazolone is taken as evidence that it is the *trans*-form; it follows that the product obtained by the action of phenylhydroxylamine on ethyl hydroxymethylenephénylacétate, which immediately gives the isooxazolone, is the *cis*-form. When the above *trans*- $\beta$ -phenylhydroxylaminomethylenephénylacetic acid is heated above its m. p., it loses carbon dioxide, forming  $\beta$ -phenyl- $\beta$ -styrylhydroxylamine (Rupe and Wittwer, A., 1922, i, 448), which forms a somewhat unstable *dibromide*, small, white needles, m. p. 125°.

Hydroxymethylenephénylacetonitrile condenses with phenylhydroxylamine to give *phenyl- $\beta$ -cyanostyrylhydroxylamine*,  $\text{CN}\cdot\text{CPh}\cdot\text{CH}\cdot\text{NPh}\cdot\text{OH}$ , golden-yellow needles, m. p. 155°. Attempts to hydrolyse the nitrile to an acid were unsuccessful. Hydroxymethylenephénylacetonitrile condenses with aniline to form an *anilino*-derivative,  $\text{NHPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CN}$ , white needles, m. p. 156°; with phenylhydrazine to a *phenylhydrazino*-derivative, white needles, m. p. 155–156°; and with *p*-aminophenol to form a *p*-hydroxyanilino-derivative, greyish-green needles, m. p. 150°. The last forms a *copper* salt,  $(\text{C}_{15}\text{H}_{11}\text{ON}_2)_2\text{Cu}$ , a nearly black powder.

E. H. R.

**The Interaction of Aliphatic Alcohols and  $\beta$ -Dibromopropylthiocarbimide.** RAYMOND M. HANN (*J. Amer. Chem. Soc.*, 1923, 45, 482–486).—Dixon (T., 1892, 61, 545; 1895, 67, 564; 1896, 69, 22) records the formation of 5-bromo-2-alkyloxy-4:6-dihydro-1:3-thiazines by the action of aliphatic alcohols on dibromopropylthiocarbimide. Gabriel (A., 1906, i, 889) considered these compounds to be 2-alkyloxy-5-bromomethyl- $\Delta^2$ -thiazolines. From a consideration of the reaction of *n*-butyl and isopentyl alcohols with the thiocarbimide and from a crystallographic study of the products, the author is of the opinion that the product formed in every case, regardless of the aliphatic alcohol used, is 2-hydroxy-5-bromomethyl- $\Delta^2$ -thiazoline, m. p. 95–96°. Secondary alcohols appear to react similarly. W. G.

**Halogenated Derivatives of Ketodihydro-1:4-benzthiazines and the Products of their Transformations. Conversion of Thiazine into Thiazole Compounds.** K. ZAHN (*Ber.*, 1923, 56, [B], 578–587).—Ketodihydro-1:4-benzthiazines react readily with halogens to yield mono- and di-substituted derivatives, in which the halogen atoms are highly reactive. In the case of the dichloro-compounds, there is a remarkable tendency for the thiazine to contract to the thiazole ring.

The monohalogenated derivatives are obtained by the action of the requisite quantity of bromine, sulphuryl chloride, or gaseous chlorine on a solution of the thiazine in the necessary amount of boiling benzene. 2-Bromo-3-keto-2:3-dihydro-1:4-benzthiazine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{CHBr} \end{smallmatrix}$ , colourless crystals, decomp. about 220° after

previous darkening; 2-chloro-3-keto-2:3-dihydro-1:4-benzthiazine, decomp.  $215^{\circ}$ ; 2:7-dichloro-3-keto-5-methyl-2:3-dihydro-1:4-benzthiazine, decomp. about  $245^{\circ}$  after darkening at  $200^{\circ}$ , and 2-chloro-3-keto-2:3-dihydro- $\alpha$ -naphththiazine, gradual decomp. above  $200^{\circ}$ , are described. When boiled with the requisite alcohol, the halogenated compounds exchange the halogen atom for the alkoxy-group. The following compounds are obtained in this manner: 2-methoxy-3-keto-2:3-dihydro-1:4-benzthiazine, almost colourless leaflets, m. p.  $188-189^{\circ}$ ; 2-ethoxy-3-keto-2:3-dihydro-1:4-benzthiazine, colourless crystals, m. p.  $168-169^{\circ}$ ; 7-chloro-2-methoxy-3-keto-5-methyl-2:3-dihydro-1:4-benzthiazine, pale brown prisms, m. p.  $189-190^{\circ}$ , and the corresponding ethoxy-derivative, colourless needles, m. p.  $197^{\circ}$ ; 2-methoxy- and 2-ethoxy-3-keto-2:3-dihydro- $\alpha$ -naphththiazine, prisms, m. p.  $223-224^{\circ}$ , and lustrous leaflets, m. p.  $208-209^{\circ}$ , respectively. These compounds are soluble in alkali hydroxide solutions with the formation of salts of the enolic forms which, however, could not be isolated. 2-Methoxy-3-keto-2-methyl-2:3-dihydro-1:4-benzthiazine, long, colourless needles, m. p.  $80-81^{\circ}$ , is prepared by the action of sodium hydroxide and methyl sulphate on the 2-methoxy-compound. 2-Acetoxy-3-keto-2:3-dihydro-1:4-benzthiazine, colourless, prismatic crystals, m. p.  $172-173^{\circ}$ , is obtained by the action of sodium acetate dissolved in glacial acetic acid on the 2-chloro-derivative; it is converted by sulphuric acid in the presence of ethyl alcohol into 2-ethoxy-3-keto-2:3-dihydro-1:4-benzthiazine and by concentrated sulphuric acid at about  $50^{\circ}$  into the ether,  $(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{S}-\text{CH}_2 \end{smallmatrix})_2\text{O}$ ,

a colourless powder, decomp. above  $300^{\circ}$ .

The following dichloro-derivatives are prepared by the gradual addition of sulphuryl chloride to a solution of the requisite thiazine in nitrobenzene and subsequently heating the mixture at about  $60^{\circ}$  until hydrogen chloride ceases to be evolved: 2:2-dichloro-3-keto-2:3-dihydro-1:4-benzthiazine, colourless needles, m. p.  $195-196^{\circ}$ ; 2:2:7-trichloro-5-methyl-3-keto-2:3-dihydro-1:4-benzthiazine, m. p.  $205-206^{\circ}$ ; 2:2-dichloro-3-keto-2:3-dihydro- $\alpha$ -naphththiazine, a pale yellow, crystalline powder, decomp. about  $240^{\circ}$  after previous darkening. Cautious treatment of the dichloro-compounds with methyl alcohol leads to the isolation of 2:2-dimethoxy-3-keto-2:3-dihydro-1:4-benzthiazine, colourless crystals, m. p.  $129-130^{\circ}$ ; 7-chloro-2:2-dimethoxy-3-keto-2:3-dihydro-1:4-benzthiazine, prisms, m. p.  $203-204^{\circ}$ , and 2:2-dimethoxy-3-keto-2:3-dihydro- $\alpha$ -naphththiazine, pale yellow prisms, m. p.  $171-172^{\circ}$ , whereas under more drastic treatment methyl benzthiazole-2-carboxylate,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Me}$ , and methyl  $\alpha$ -naphththiazole-2-carboxylate, needles, m. p.  $119^{\circ}$ , are produced. Boiling ethyl alcohol transforms the dichloroketothiazine into ethylbenzthiazole-2-carboxylate, m. p.  $70-71^{\circ}$ . Ethyl 6-chloro-4-methylbenzthiazole-2-carboxylate crystallises in colourless needles, m. p.  $97-98^{\circ}$ ; the corresponding amide, colourless leaflets, m. p.  $250-251^{\circ}$ , and acid, m. p.  $140^{\circ}$ , are described. Ethyl  $\alpha$ -naphththiazole-

carboxylate forms pale yellow needles, m. p. 129—130° (amide, n. p. 253—254°; corresponding acid, m. p. 140°).

2:2-Dichloro-3-keto-2:3-dihydro-1:4-benzthiazine is converted by cold concentrated sulphuric acid or, preferably, by boiling glacial acetic acid into 2:3-diketodihydro-1:4-benzthiazine,

$\text{H}_2\text{N} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{CO} \end{array}$ , pale yellow prisms, m. p. 250° (decomp.). The

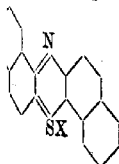
liketone is converted by dilute alkali hydroxide solutions into  $\alpha$ -thiolphenyloxamic acid,  $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , and finally into  $\alpha$ -aminophenylmercaptan and oxalic acid. It is transformed by aniline into benzthiazole-2-carboxyanilide, m. p. 157—158°, and by phenylhydrazine into benzthiazole-2-carboxyphenylhydrazide, pale yellow needles or coarse crystals, m. p. 220—222° after previous softening. 7-Chloro-2:3-diketo-5-methyldihydro-1:4-benzthiazine, n. p. 255° (decomp.), and 2:3-diketodihydro- $\alpha$ -naphthathiazine, yellow needles, decomp. 315°, are described.

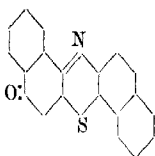
The dichloroketothiazines react with great readiness with amines, hydrazines, and phenylhydrazine. Thus, 2:2-dichloro-3-keto-2:3-dihydro-1:4-benzthiazine and aniline yield 2:3-diketodihydro-1:4-benzthiazine-2-anil, pale yellow, lustrous leaflets, m. p. 254—256°, which is converted by boiling alcohol into benzthiazole-2-carboxyanilide, m. p. 157—158°. In a similar manner, 7-chloro-5-methyldiketodihydro-1:4-benzthiazine-2-anil, golden-yellow leaflets, m. p. 247—248°, gives 6-chloro-4-methylbenzthiazole-2-carboxyanilide, colourless needles, m. p. 140—141°, and diketodihydro- $\alpha$ -naphthathiazine-2-anil, m. p. 290—292°, yields  $\alpha$ -naphthathiazole-2-carboxyanilide, colourless needles, m. p. 202—203°. 2:3-Diketodihydro-1:4-benzthiazine-2-phenylhydrazone crystallises in lustrous leaflets, m. p. 270—272° (decomp.); the corresponding zine is an orange-red powder.

2:2-Dichloro-3-keto-2:3-dihydro-1:4-benzthiazine is transformed by oxythionaphthen into the dye,  $\text{NH} \cdot \text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{S} \quad \text{C} \cdot \text{C} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{S} \quad \text{CO} \end{array} \text{C}_6\text{H}_4$ , identical with the substance prepared by Herzog (A., 1920, i, 182) in a different manner. H. W.

**Azthionium Salts of the Naphthalene Series. II.** F. KREHMANN, ALFRED GRESSLY, WLADIMIR CHIFFÈRE, and MARIE RAMM (Ber., 1923, 56, [B], 649—654).—A continuation and amplification of previous work (cf. A., 1902, i, 566; 1921, i, 449).

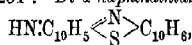
Thio- $\alpha\beta$ -dinaphthylamine (cf. Gressly, Diss., Geneva, 1902) pale, orange-yellow prisms, m. p. 185—186°, is prepared by the action of sulphur on  $\alpha\beta$ -dinaphthylamine at a temperature not exceeding 240°. It is readily converted by the action of the requisite acid in the presence of a suitable oxidising agent into di- $\alpha\beta$ -naphthazthionium salts (annexed formula), of which the nitrate (+H<sub>2</sub>O), bronze crystals, the perchlorate, dark-violet crystals, and the picrate, dark-violet needles, are described in detail. Oxidation of thio- $\alpha\beta$ -dinaphthylamine by ferric chloride





leads to the formation of *di- $\alpha$ -naphthathiazine* (annexed formula), lustrous, dark brownish-red needles, m. p. 256—257°.

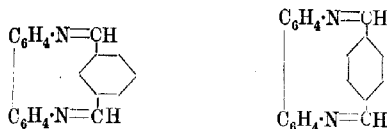
Thiodi- $\alpha$ -naphthylamine (cf. Kehrman and Dardel, A., 1922, i, 1064), m. p. 164—166°, in a capillary filled with carbon dioxide, is oxidised with great readiness in substance or in solution to  $\alpha$ -dinaphthathiazone (cf. A., 1902, i, 566). It is converted by acetic anhydride and anhydrous zinc chloride into the *acetyl* derivative,  $C_{20}H_{12}SNAc$ , colourless crystals, m. p. 214—215°. *Di- $\alpha$ -naphthazthionium nitrate*, brown needles, *perchlorate*, and *ferri chloride*,  $C_{20}H_{12}NSCl_4Fe$ , are described. The salt last mentioned is transformed by aniline hydrochloride and aniline in the presence of alcohol (80%) into *di- $\alpha$ -naphthathiazone* and *N-phenyldi- $\alpha$ -naphthathiazime*,  $PhN:C_{10}H_5 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} C_{10}H_5$ , small lustrous black crystals, m. p. 250—254°. *Di- $\alpha$ -naphthathiazime*,



yellowish-red crystals, gives a dark, violet-brown *chloroplatinate*, a bluish-violet *hydrochloride*, and a *perchlorate*. H. W.

**Influence of Substitution in the Components on Equilibrium in Binary Solutions. XXXVIII. The Binary Systems of Trinitrobenzene and Trinitrotoluene with the Three Isomeric Phenylenediamines.** ROBERT KREMANN and OTTO MAUERMANN (*Monatsh.*, 1923, 43, 315—320).—Both trinitrobenzene and trinitrotoluene form equimolecular compounds with each of the phenylenediamines. For 1:3:5-trinitrobenzene and *o*-phenylenediamine, the equimolecular compound melts at 163° (33.7% by weight of diamine), the eutectic between the compound and diamine occurs at 92° and 93% of the diamine, that between the compound and trinitrobenzene occurring at 108° and 3% of diamine. The six corresponding figures for the other binary systems examine are as follows: 2:4:6-Trinitrotoluene and *o*-phenylenediamine 97.5° (32.3%), 83° (57%), and 65° (9%). 1:3:5-Trinitrobenzene and *m*-phenylenediamine, 168° (33.7%), 45° (82%), and 105° (7%). 2:4:6-Trinitrotoluene and *m*-phenylenediamine, 105° (32.3%), 51.5° (90.5%), and 70° (6%). 1:3:5-Trinitrobenzene and *p*-phenylenediamine, 145.5° (33.7%), 106° (64%), and 101.5° (9%). 2:4:6-Trinitrotoluene and *p*-phenylenediamine, 93° (32.3%), 88° (38%), and 64° (8%). The results fall in line with those previously obtained with dinitrobenzenes, taking into account the effect of third nitro-group (cf. A., 1919, ii, 54). E. E. T.

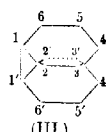
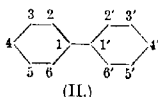
**The Structure of Benzidine.** ROGER ADAMS, J. E. BULLOCK and W. C. WILSON (*J. Amer. Chem. Soc.*, 1923, 45, 521—527).—It has been found that benzidine and certain of its derivatives condense readily with meta- and para-disubstituted benzene compounds, namely with terephthalaldehyde and isophthalaldehyde, to form substances which presumably have the structures



These compounds are characterised by their extreme insolubility and high melting or decomposition points. Their analysis is difficult, because the moment the combustion starts all the material is burned at once. Benzidine gives with *isophthalaldehyde* an amorphous compound,  $\text{C}_6\text{H}_4\text{N}=\text{CH}$   $\text{C}_6\text{H}_4\text{N}=\text{CH}$   $\text{C}_6\text{H}_4$ , with *terephthalaldehyde*

a yellow compound, and with *terephthalaldehyde monazine*, m. p.  $232^\circ$ , an orange-coloured compound. Dianisidine gives with *terephthalaldehyde* a yellowish-green compound. *Terephthalaldehyde dihydrazone*, m. p.  $165^\circ$ , was obtained by treating *terephthalaldehyde* with an excess of hydrazine hydrate.

From the above results it seems probable that the benzene rings in diphenyl derivatives are in motion within the limiting positions of the two possible Kaufer formulæ, I and III (cf. A., 1907, i, 307, 794), and the intermediate position, II, which is usually assigned to diphenyl.



W. G.

**Interaction of Formaldehyde and the Nitronaphthylamines.** GILBERT T. MORGAN and FRANK RAYMOND JONES (*J. Soc. Chem. Ind.*, 1923, 42, 92—97r).—The condensation of formaldehyde with each of the known nitronaphthylamines has been investigated in order to determine the effect of orientation of the substituent groups on the reactivity of the amines towards formaldehyde. The simplest form of condensation occurs with 1-nitro-3-naphthylamine, a methylene group becoming associated with two imino-groups from the primary nitroamine, producing *methylene-bis-1-nitro-3-naphthylamine*, which exists as two chromo-isomerides having the same melting point,  $222-223^\circ$ . The yellow isomeride, obtained as needles when the condensation is effected in glacial acetic acid, is transformed by solution in hot pyridine into the red form, which crystallises in hard, bright red prisms. With 4-nitro- $\alpha$ -naphthylamine, in cold glacial acetic acid, formaldehyde condenses to form 4:4'-dinitro-1:1'-diamino-2:2'-dinaphthylmethane, m. p.  $268-270^\circ$  (decomp.), in which the methylene group has probably entered the ring in the remaining reactive position 2. The product is soluble in hot nitrobenzene, from which it crystallises on cooling as yellow needles. An analogous condensation occurs, but less readily, with 2-nitro- $\alpha$ -naphthylamine,

leading to the production of 3:3'-*dinitro*-4:4'-*diamino*-1:1'-*dinaphthylmethane*, m. p. 299—301° (decomp.). The product dissolves readily in nitrobenzene, from which it crystallises in fine, silky, voluminous, rectangular, golden-yellow prisms. With the heteronuclear nitronaphthylamines, the condensations are more complicated and comparable with the reactions arising in the case of the unsubstituted naphthylamines (Morgan, T., 1898, 73, 536; Senier and Goodwin, 1902, 81, 288; Möhlau and Haase, A., 1903, i, 118, 126). The condensation of 5-nitro- $\beta$ -naphthylamine with formaldehyde in cold alcohol probably results in the production of *methylenebis*-5-nitro- $\beta$ -naphthylamine and 5:5'-*dinitro*-2:2'-*diamino*-1:1'-*dinaphthylmethane*, m. p. 233—235°. The methylene base, the primary condensation product, was not isolated in a state of purity, but the succeeding products were obtained separately by effecting the condensation in alcohol in the presence of mineral acid. On prolonged heating, 5:5'-*dinitro*-2:2'-*diamino*-1:1'-*dinaphthylmethane* was further condensed to the corresponding dihydronaphthacridine, which by aerial oxidation was converted into 4:10-*dinitrodinaphthacridine*. Experiments with 8-nitro- $\beta$ -naphthylamine indicate that, in position 8, the nitro-group appears to exert steric hindrance on the entry of the methylene radicle into the ring, so that the primary condensation product, *methylenebis*-8-nitro- $\beta$ -naphthylamine, m. p. 178°, appears in alcoholic solution, but in alcohol acidified with hydrochloric acid the reaction proceeds to the production of a small yield of 8:8'-*dinitro*-2:2'-*diamino*-1:1'-*dinaphthylmethane*. The behaviour of 8-nitro- $\alpha$ -naphthylamine is similar to that of the corresponding  $\beta$ -naphthylamine. In glacial acetic acid, 5:5'-*dinitro*-4:4'-*diamino*-1:1'-*dinaphthylmethane* is produced and separates out with three molecular proportions of formaldehyde, as a pale yellow, crystalline powder. The yield is almost quantitative, and the m. p. of the additive compound is 172—173°. 5-Nitro- $\alpha$ -naphthylamine resembles  $\alpha$ -naphthylamine in condensing with formaldehyde to give ill-defined and inseparable products. Evidence was obtained of the presence in the condensed products of a hydrolysable methylene base and a base of the dinaphthacridine series. J. S. G. T.

**Action of the Oxides and the Oxy-acids of Nitrogen on the Phenylcarbamides.** HUGH RYAN and PETER K. O'TOOLE. (*Proc. Roy. Dublin Soc.*, 1923, 17, 139—155; cf. this vol., 321, 322, 323).—The nitration of phenylcarbamide, *s*-diphenylcarbamide, *as*-diphenylcarbamide, and triphenylcarbamide has been systematically investigated. In regard to ease of nitration, the phenylcarbamides resemble the corresponding phenylurethanes; they are much less easily nitrated than the analogous phenyl nitrosoamines.

When treated with cold dilute nitric acid, phenylcarbamide forms its nitrate; *s*- and *as*-diphenylcarbamides are unchanged; and triphenylcarbamide yields a *dinitrotriphenylcarbamide*, yellow prisms, m. p. 190—191°, and a *trinitrotriphenylcarbamide*, slightly yellow leaves, m. p. 205—206°. Under similar conditions, but in

carbon tetrachloride suspension, phenylcarbamide forms the nitrate, *p*-nitro-, and 2:4-dinitro-derivatives; *s*-diphenylcarbamide is nitrated to the 4-nitro-, 4:4'-dinitro-, and 2:4:2':4'-tetranitro-derivatives; from *as*-diphenylcarbamide no pure compound is obtained; triphenylcarbamide gives the above dinitro- and trinitro-compounds, and a *pentanitrotriphenylcarbamide*, yellow prisms, decomp. 180°, m. p. 235—236° (decomp.). Cold fuming nitric acid converts phenylcarbamide into 2:4-dinitrophenylnitrocarbamide; *s*-diphenylcarbamide forms the 4:4'-dinitro- and 2:4:2':4'-tetranitro-derivatives; whilst both *as*-diphenylcarbamide and triphenylcarbamide give 2:4:2':4'-tetranitrodiphenylamine.

In cold glacial acetic acid solution, nitrous acid converts phenylcarbamide into nitrosophenylcarbamide, whilst *as*-diphenylcarbamide and triphenylcarbamide are apparently not acted on. *s*-Diphenylcarbamide forms *dinitroso-s-diphenylcarbamide*, prismatic needles, decomp. 103°, which is converted on being boiled with alcohol into *s*-diphenylcarbamide, gives 2:4:2':4'-tetranitro-*s*-diphenylcarbamide on direct nitration, and with nitric acid in acetic acid solution gives 4:4'-dinitro-*s*-diphenylcarbamide. A synthesis of the latter by the condensation of 1 mol. of carbamide with 2 mols. of *p*-nitroaniline is described. The same dinitroso-compound is produced by the action of nitrous fumes in acetic acid solution on *s*-diphenylcarbamide, but by the prolonged action of nitrogen peroxide, 4:4'-dinitrodiphenylcarbamide is produced. Phenylcarbamide is converted by nitrous fumes in carbon tetrachloride suspension into *o*-nitrophenol and *p*-nitrophenol. *as*-Diphenylcarbamide is decomposed by nitrogen peroxide at the ordinary temperature, forming 4:4'-dinitrodiphenylnitrosoamine; triphenylcarbamide under similar conditions gives the trinitrotriphenylcarbamide (above).

W. S. N.

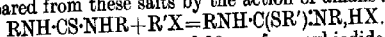
**Action of the Oxides and the Oxy-acids of Nitrogen on Phenylmethylcarbamide.** HUGH RYAN and MICHAEL J. SWEENEY (*Proc. Roy. Dublin Soc.*, 1923, 17, 157—162; cf. preceding abstract).—No nitro-derivatives of phenylmethylcarbamide have been obtained, because nitrous acid converts phenylmethylcarbamide into methylaniline; nitro-derivatives of the latter are in all cases isolated.

Nitrous acid converts phenylmethylcarbamide into gaseous nitrogen peroxide converts phenylmethylcarbamide into 4:6-trinitrophenylmethylnitrosoamine (tetryl), but in solution 4:6-trinitrophenylmethylnitrosoamine, 2:4-dinitro-, and 2:4:6-trinitromethylaniline are successively produced. In the presence of carbamide nitrate, nitric acid has little, if any, action on phenylmethylcarbamide, but in the presence of nitrous acid, phenylmethylnitrosoamine, 4-nitrophenylmethylnitrosoamine, 2:4-dinitromethylaniline, 2:4:6-trinitromethylaniline, and tetryl are formed.

Tetryl may readily be obtained pure by the nitration of phenylmethylcarbamide or of phenylmethylnitrosoamine.

W. S. N.

**Thiocarbamide Ethers.** F. B. DAINS and W. C. THOMPSON (*Univ. Kansas Sci. Bull.*, 1922, 13, 118—120; cf. Will, A., 1881, 905; Will and Bielschowski, A., 1882, 1090; Evers, A., 1888, 600; Foerster, A., 1888, 944).—Substituted thiocarbamides form additive products with alkyl halides, the free thiocarbamide ethers being prepared from these salts by the action of alkalis:

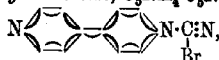


When 15 g. of thiocarbamilide and 10 g. of propyl iodide are heated for one hour on the steam-bath, a light brown, viscous liquid separates and solidifies on cooling. When crystallised from alcohol, colourless *N*-diphenyl-*S*-propylthiocarbamide hydriodide, m. p. 103°, is obtained; the free base forms needles, m. p. 61.5°. Butyl iodide and thiocarbamilide yield *N*-diphenyl-*S*-butylthiocarbamide hydriodide, m. p. 122°, which could not be crystallised, but was well washed with ethyl ether; the corresponding base is a colourless oil. Propyl iodide and di-*p*-tolylthiocarbamide give *N*-di-*p*-tolyl-*S*-propylthiocarbamide hydriodide, m. p. 165° (base, fine, white needles, m. p. 99°). The corresponding butyl derivative is a thick, colourless liquid (hydriodide, m. p. 145°). Di-*m*-xylylcarbamide and propyl iodide yield directly *N*-di-*m*-xylyl-*S*-propylphenylthiocarbamide, m. p. 113.5°. The unsymmetrical nature of the molecule did not prevent addition of the alkyl iodide, since methyl iodide and phenylbromophenylthiocarbamide yield *N*-phenyl-*p*-bromophenyl-*S*-methylthiocarbamide hydriodide, m. p. 152° (base, white needles, m. p. 79°); *N*-phenyl-*p*-bromophenyl-*S*-propylthiocarbamide hydriodide, a red oil (base, m. p. 84°), and *N*-phenyl-*p*-bromophenyl-*S*-butylthiocarbamide hydriodide, a thick oil (base, a viscid oil) were also prepared. When phenylthiocarbamide and butyl iodide are warmed together on a water-bath, a gummy mass is produced which on treatment with sodium carbonate yields *N*-phenyl-*S*-butylthiocarbamide, a heavy oil.

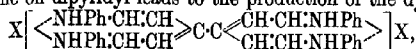
## CHEMICAL ABSTRACTS.

**The Presumed Reaction of 4 : 4'-Dipyridyl with Potassium Ferrocyanide.** J. P. WIBAUT and ELISABETH DINGEMANSE (*Rec. trav. chim.*, 1923, 42, 184—185).—It has been stated that 4 : 4'-dipyridyl gives a characteristic blue precipitate with potassium ferrocyanide (Anderson, *Annalen*, 1870, 78, 274; Weidel and Russo, A., 1883, 483), and Heuser and Stoehr obtained reddish-brown crystals which they assert, apparently without experimental evidence, to be 4 : 4'-dipyridyl ferrocyanide (A., 1892, 75). The authors have prepared the blue precipitate and found it to be Berlin-blue, whilst the reddish-brown crystals obtained in hydrochloric acid solution are now proved to be the dipyridyl ferrocyanide. The reaction, however, is not specific for 4 : 4'-dipyridyl.  
H. J. E.

**Fission of 4 : 4'-Dipyridyls by Cyanogen Halides.** W. KÖNIG [with G. EBERT and K. CENTNER] (*Ber.*, 1923, 56, [B], 751—758).—The action of cyanogen bromide and amines on 4 : 4'-dipyridyl has been investigated with the object of preparing pentamethin dyes.

4:4'-Dipyridyl 1-cyanobromide,  $C_5NH_4 \cdot C_5NH_4Br \cdot CN$ , or

is prepared by the addition of an ethereal solution of cyanogen bromide to 4:4'-dipyridyl dissolved in alcohol; the use of anhydrous materials and the exclusion of moisture are essential to the success of the preparation, the special apparatus for which is fully described in the original. The substance forms a pale brown precipitate which decomposes into dipyridyl and cyanogen bromide when heated. It gives salts with picric acid and sodium perchlorate. It is converted by aniline and subsequent treatment with sodium perchlorate, picric acid, or potassium iodide into the corresponding dipyridyl, salts of which the iodide,  $C_{20}H_{18}N_4I_2 \cdot H_2O$ , brownish-yellow leaflets which commence to sublime at  $65^\circ$ , is described in detail. The simultaneous action of cyanogen bromide and aniline on dipyridyl leads to the production of the dye



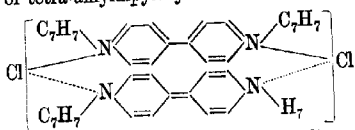
which is converted into 1:1'-diphenyl-4:4'-dipyridylium bromide; the corresponding perchlorate,  $C_{22}H_{18}O_8N_4Cl_2$ , pale, greenish-yellow needles, m. p.  $299^\circ$  (decomp.), the picrate,  $C_{34}H_{22}O_{14}N_8$ , slender, yellow needles, m. p.  $170^\circ$ , and the chloroferrate,  $C_{22}H_{18}N_4Cl_2Fe_3$ , small, yellow needles, m. p.  $210-215^\circ$ , are described. 1:1'-Diphenyl-4:4'-dipyridylium di-iodide is precipitated as a yellow, unstable polyhydrate which passes into the stable salt ( $+0.5H_2O$ ), small, dark red prisms.

The 1:1'-diphenyldipyridylium salts exhibit the "triphenylmethyl phenomenon" particularly distinctly when they are warmed with zinc dust and glacial acetic acid; the deep bluish-green coloration disappears immediately when the solutions are shaken with air, and the process may be repeated as long as unused zinc dust is present. The same change is observed in aqueous-alcoholic solution in the presence of hyposulphite, zinc dust, or ferrous sulphate, or in aqueous solution in the presence of free hydroxylamine; a merquinonoid compound appears to be thereby produced (cf. Emmert, A., 1922, i, 1064). A pure green coloration is caused by the addition of alkali hydroxide to aqueous solutions of 1:1'-diphenyldipyridylium salts; its formation is explained on the assumption that the ammonium base is partly converted into the pseudobase, which passes into a mixture of 1:1'-diphenyl-2:2'-dipyridone and 1:1'-diphenyl-2:2'-tetrahydro-4:4'-dipyridyl; the latter substance becomes tautomerised to the 4:4'-tetrahydro-compound which reacts with unchanged ammonium base to give a green, quinhydrone-like compound.

H. W.

**Quinhydrone-like Compounds of 1:1'-Dialkyldihydro-4:4'-dipyridyls.** BRUNO EMMERT and OTTO VARENKAMP (*Ber.*, 1923, 56, [B], 491-501).—In a previous communication (A., 1922, i, 1064), it has been shown that 4:4'-dipyridyl dibenzyl-iodide is reduced by 1:1'-dibenzyltetrahydro-4:4'-dipyridyl to

1:1'-dibenzylidihydro-4:4'-dipyridyl, which immediately unites with a second molecule of dipyridyl dibenzyl iodide to give a quinhydrone-like compound. More recently, Dimroth and Frister (this vol., i, 149) have isolated the parent substance of this quinhydrone, which they term dipyridylviolet chloride. In the present communication, this nomenclature is adopted, and a further series of tetra-alkyldipyridylviolet halides is described.



*Tetrabenzylidipyridylviolet chloride* (annexed formula), violet, oblique leaflets, m. p. about 190° (decomp.), when rapidly heated, is prepared by the action of an alcoholic solution of 1:1'-dibenzyltetrahydro-4:4'-dipyridyl on an equimolecular quantity of dipyridyl dibenzylchloride. It can be preserved during some days when exposed to air. It is extraordinarily sensitive to air if dissolved in acetic anhydride or glacial acetic acid, but much more stable in chloroform, acetone, aniline, or, particularly, in pyridine.

*Tetrabenzylidipyridylviolet bromide*, dark violet, oblique leaflets, is prepared in a similar manner. The substance is also prepared by the reduction of 4:4'-dipyridyl dibenzylbromide in alcoholic solution (90%) by zinc dust or magnesium powder, thus indicating that the blue colour observed during the treatment of dipyridyl dialkyl iodides with zinc dust is due to the quinhydrone, and not, as Weitz and König have supposed (A., 1922, i, 1186), to the halogen-free, 1:1'-dialkyl-4:4'-dipyridinium radicle.

[With VALENTIN DÖLLEIN.]—*Tetraisoamylidipyridylviolet iodide*, dark violet leaflets, with a metallic reflex, is prepared by the action of zinc dust on 4:4'-dipyridyl diisoamyl iodide.

4:4'-Dipyridyl dibenzylchloride is reduced by chromous chloride to tetrabenzylidipyridylviolet chloride; the corresponding bromide is produced in unsatisfactory yield by the action of phenylhydrazine on 4:4'-dipyridyl dibenzylbromide.

The semiquinonoid character of tetrabenzylidipyridylviolet bromide and iodide is further established by the observation that a molecular proportion of either substance dissolved in glacial acetic acid absorbs an atomic proportion of oxygen.

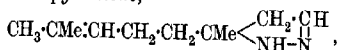
[With HEINRICH LUDWIG.]—2:6:2':6'-*Tetradimethylidipyridyl dibenzyl iodide*, obtained from its components at 150°, is isolated in a red, anhydrous and a yellow, hydrated form. It is converted by dibenzyltetrahydrodipyridyl into *tetrabenzylidipyridylviolet iodide*, dark bronze-brown, oblique leaflets, m. p. about 170°. 2:6-Dimethylpyridine benzyl iodide is prepared from its components at 130° (corresponding perchlorate, long needles, m. p. 141°); it is reduced by sodium amalgam to *dibenzyltetrahydrodi-2:6:2':6'-tetramethylpyridyl*, pointed prisms, m. p. 124°, after previous darkening.

[With GERHARD JUNGCK.]—Dimethyltetrahydrodicollidyl and dipyridyl dibenzyl iodide yield tetrabenzylidipyridylviolet iodide and methylocollidinium iodide. Collidinium methoperchlorate is

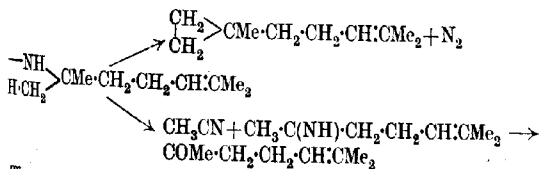
obtained by the action of silver nitrate dissolved in alcohol on 1:1'-dimethyltetrahydrodicollidyl and, after removal of the silver, addition of perchloric acid.

[With EBERHARD VOGT.]—By the introduction of a phenyl group in position 4, it was hoped to weaken the union of the  $\gamma$ -carbon atoms possibly to such an extent as to lead to the formation of the radicle. With this object, 4-phenylpyridine is converted into the corresponding *methiodide*, almost colourless crystals, which, however, is reduced by sodium amalgam and water to 4-phenyl-1-methyldihydropyridine, colourless needles, m. p.  $36^\circ$ , instead of the expected dipyrldyl derivative. H. W.

**The Conversion of Citral into the Hydrocarbon, C<sub>10</sub>H<sub>18</sub>, of the cycloPropane Series.** N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 1—19; A., 1911, i, 1027; 1914, i, 129).—The hydrazone of citral is converted by distillation into the pyrazolone. The anomalous behaviour of citral in forming a semi-stable hydrazone, although it has a double bond in the  $\alpha\beta$ -position to the carbonyl group, which seems usually to preclude the formation of hydrazones, giving in their place pyrazolones, is explained as being due to the space configuration of the citral, which approaches that of ring compounds, these giving stable hydrazones. *Citralpyrazolone*,

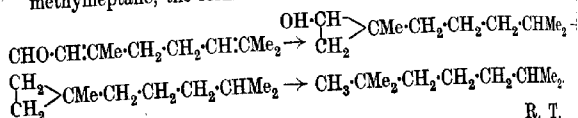


is obtained as an oil, b. p.  $122^\circ/12$  mm.,  $d_4^{20}$  0.9213,  $n_D^{20}$  1.4897, soluble in water, and very hygroscopic. The *phenylthiocarbamyl* compound,  $\text{NHPh}\cdot\text{CS}\cdot\text{N}_2\text{C}_{10}\text{H}_{17}$ , forms large prisms, m. p.  $51^\circ$ . The pyrazolone is unaffected by cold glacial acetic acid or by colduming hydrochloric acid, but on heating with the latter in a sealed tube at  $100^\circ$ , hydrazine hydrochloride is eliminated, and *p*-cymene obtained quantitatively. The *p*-cymene thus obtained is uncontaminated by other products, and this method is recommended for its preparation in a pure state. Citral itself gives the same product under these conditions, but the reaction is much slower, and it seems probable that the pyrazolone is converted directly into *p*-cymene, and not first into citral. The pyrazolone on distillation, in the presence of platinum catalyst, from alkali hydroxide, gives in the distillate, together with unchanged material, acetone, nitrile, methylheptanone, and 1-methyl-1-isohexylenylcyclopropane, C<sub>10</sub>H<sub>18</sub>, formed in the following way:



The hydrocarbon had b. p.  $160^\circ/735$  mm.,  $d_4^{20}$  0.7744,  $n_D^{20}$  1.4432. A structure was deduced from its oxidation products, acetone, a

ketone, and an acid. The ketone,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CHMe}_2$ , has m. p. 14.5—15°, b. p. 222.5°/749 mm.,  $d_4^{20}$  0.9406,  $n_D^{20}$  1.4491 (*semi-carbazone*, m. p. 149—151°). The acid,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , has b. p. 219—222°/756 mm.,  $d_4^{15}$  0.9919,  $n_D^{15}$  1.4444, and gives an anilide, m. p. 126—127°. Further evidence of the structure of the hydrocarbon is given by its reduction products, obtained by the action of hydrogen in the presence of a platinum catalyst. This results in a mixture of three parts of 1-methyl-1- $\beta$ -methylpentyl-cyclopropane with five parts of a further reduction product,  $\beta\beta$ -trimethylheptane, b. p. 150.5—151.5°/748 mm.,  $d_4^{20}$  0.7215,  $n_D^{20}$  1.400. The reduction of the undistilled hydrazone, which has a citral-like structure, leads to the production of an isomeride of the latter,  $\beta$ -dimethyloctane. It is shown that the hydrocarbon obtained by Skita and Ritter (A., 1911, i, 272) by the Sabatier reduction of citral is not, as they stated, the  $\beta$ -dimethyloctane, but  $\beta\beta$ -trimethylheptane, the formation of which is thus explained:



R. T.

**Bromo-derivatives of 4-Methylglyoxaline.** FRANK LEE PYMAN and GEOFFREY MILLWARD TIMMS (T., 1923, 123, 494—503).

**4(5)-Nitroglyoxaline-5(4)-carboxylic Acid.** A. WINDAUS and W. LANGENBECK (*Ber.*, 1923, 56, [B], 683—686).—The acid (cf. Windaus and Opitz, A., 1911, i, 752; Mömer, A., 1918, i, 198; Z. *physiol. Chem.*, 1918, 103, 80; Fargher and Pyman, T., 1919, 115, 219) may be obtained readily by the condensation of 5(4)-nitro-4(5)-methylglyoxaline with aldehydes and oxidation of the products by potassium permanganate.

4(5)-Nitro-5(4)-methylglyoxaline condenses with benzaldehyde in the presence of piperidine at 150—160° to yield 4(5)-nitro-5(4)-styrylglyoxaline,  $\begin{matrix} \text{N} \cdot \text{C}(\text{NO}_2) \\ | \\ \text{CH} - \text{NH} \end{matrix} > \text{C} \cdot \text{CH} \cdot \text{CHPh}$ , golden-yellow leaflets,

decomp. above 220°; the corresponding compound from anisaldehyde crystallises in orange-yellow needles, m. p. about 296° (decomp.). The styryl derivative is converted by potassium permanganate in cold alkaline solution almost quantitatively into 4(5)-nitroglyoxaline-5(4)-carboxylic acid, almost colourless prisms m. p. above 300° (decomp.). The acid loses carbon dioxide when heated at 150° and yields 4(5)-nitroglyoxaline. *Methyl-4(5)-nitroglyoxaline-5(4)-carboxylate* crystallises in colourless, lustrous leaflets, m. p. 212—213°; 4(5)-nitroglyoxaline-5(4)-carboxamide forms almost colourless needles or prisms, m. p. 291°. Methyl nitroglyoxalinecarboxylate is hydrogenated in absolute alcohol

solution in the presence of palladium black to the corresponding amino-ester, which is characterised as the *picrate*,  $C_{11}H_{10}O_6N_4$ , yellow needles, m. p.  $235^\circ$  (decomp.), and *hydrochloride*,  $C_8H_8O_2N_2Cl$ , m. p. about  $210^\circ$  (decomp.). 4(5)-Aminoglyoxaline-5(4)-carboxamide is prepared in a similar manner, and is characterised as the *picrate*,  $C_{10}H_8O_6N_4$ , small prisms, decomp. about  $240^\circ$ , and the *hydrochloride*,  $C_8H_7ON_2Cl$ .  
H. W.

**Bromination of Glyoxaline-4-carboxyanilide.** HAROLD KING and WILLIAM OWEN MURCH (T., 1923, 123, 621—629).

**Some New Unsymmetrical Dialkylbarbituric Acids. I. Ethylalkylbarbituric Acids.** M. TIFFENEAU (Bull. Soc. chim., 1923, [iv], 33, 183—188).—The preparation and properties of some new ethylalkylbarbituric acids are described. *Ethyl-n-butylbarbituric acid* forms slender needles, m. p.  $128^\circ$ . It was obtained by condensing carbamide with *ethyl ethyl-n-butylmalonate*, b. p.  $240$ — $245^\circ/770$  mm. This ester on hydrolysis and subsequent heating of the free acid gives  $\alpha$ -ethylhexoic acid, b. p.  $220$ — $224^\circ/770$  mm. Its *chloride* boils at  $85$ — $90^\circ/20$  mm., and its carbamide,  $\alpha$ -ethylhexoylearbamide, melts at  $159^\circ$ . *Ethylisobutylbarbituric acid*, needles, m. p.  $174^\circ$ , was prepared in the usual way from *ethyl ethylisobutylmalonate*, b. p.  $234$ — $240^\circ/760$  mm. This ester on saponification gave *ethylisobutylmalonic acid*, m. p.  $107$ — $108^\circ$ , which by loss of carbon dioxide gave  $\gamma$ -methyl- $\alpha$ -ethylvaleric acid, b. p.  $115^\circ/20$  mm. The *chloride* of this acid boils at  $168$ — $171^\circ$  and the *amide* melts at  $89^\circ$ . Both the butyl- and isobutyl-ethylbarbituric acids are about three times as active as veronal. *Ethylisoamylbarbituric acid* forms leaflets, m. p.  $154$ — $155^\circ$ . It is nearly as powerful a hypnotic as the butyl derivatives, but acts much more rapidly, and its effect is correspondingly less prolonged. It is obtained from *ethyl ethylisoamylmalonate*, b. p.  $248$ — $253^\circ$ . *Ethylisoamylmalonic acid* melts at  $116$ — $118^\circ$ , and is converted on heating into  $\delta$ -methyl- $\alpha$ -ethylhexoic acid, b. p.  $228$ — $232^\circ$ . The *chloride* of this acid boils at  $188$ — $192^\circ$ , and the *amide* melts at  $106$ — $108^\circ$ . To complete the series of alkylbarbituric acids, *di-n-butylbarbituric acid* was prepared. It melts at  $153^\circ$ .

G. F. M.

**Some New Unsymmetric Dialkylbarbituric Acids. II. Homologous Series.** CH. SOMMAIRE (Bull. Soc. chim., 1923, [iv], 33, 189—195).—The preparation of the following ethyl dialkylmalonates, free dialkylmalonic acids, and the dialkylacetic acids derived from them, and also the dialkylbarbituric acids obtained by condensation with carbamide, are described: *Ethyl methyl-n-butylmalonate*, b. p.  $235$ — $241^\circ$ ; *methyl-n-butylmalonic acid*, m. p.  $98^\circ$ ; *methyl-n-butylbarbituric acid*, m. p.  $181^\circ$ ; *ethyl propyl-n-butylmalonate*, b. p.  $248$ — $253^\circ$ ; *propylbutylmalonic acid*, m. p.  $150$ — $151^\circ$ ;  $\alpha$ -propylhexoic acid,  $d_4^{20}$  0.914, its *chloride*, b. p.  $192$ — $195^\circ/767$  mm., and *amide*, m. p.  $122$ — $123^\circ$ ; *propylbutylbarbituric acid*, m. p.  $153^\circ$ ; *butylisobutylbarbituric acid*, m. p.  $153^\circ$ ; *ethyl methylisobutylmalonate*, b. p.  $232$ — $236^\circ$ ; *methylisobutylbarbituric*

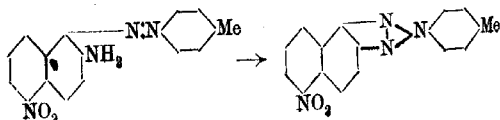
acid, m. p. 195°;  $\gamma$ -methyl- $\alpha$ -propylvaleramide, m. p. 121°; propylisobutylbarbituric acid, m. p. 164—165°; ethyl methylisocamylmalonate, b. p. 242—247°; methylisocamylmalonic acid, m. p. 131—132°;  $\alpha$ , $\delta$ -dimethylhexoic acid, b. p. 120—130°/15 mm., giving a chloride, b. p. 69—71°/15 mm., and an amide, m. p. 103°; methylisocamylbarbituric acid, m. p. 187°; ethyl propylisocamylmalonate, b. p. 254—259°/76 mm.; propylisocamylmalonic acid, m. p. 143°;  $\delta$ -methyl- $\alpha$ -propylhexoic acid, b. p. 238—245°, giving a chloride, b. p. 200—205°; and an amide, m. p. 117—118°; propylisocamylbarbituric acid, m. p. 134°; ethyl heptylmalonate, b. p. 273—275°; ethyl ethylheptylmalonate, b. p. 168—171°/15 mm.; ethyl heptylbarbituric acid, m. p. 118—119°. The maximum hypnotic activity observed by Tiffeneau (preceding abstract) with the C<sub>10</sub> and C<sub>11</sub> members of the barbituric acid series was not exceeded by any of the above homologues. The activity of the higher members seems to depend on the solubility, which diminishes rapidly with increasing number of carbon atoms. The influence of a branched chain on the solubility in water is anomalous. In the methyl series, the isobutyl group does not change the solubility as compared with the butyl group, in the ethyl series it somewhat reduces the solubility, in the propyl series it increases it slightly, and in the butyl series it considerably increases it. In all cases, an increasing number of carbon atoms decreases the solubility, with the sole exception of the methyl- and ethyl-butylbarbituric acids, the solubility of the former being only about one-half of that of the latter.

G. F. M.

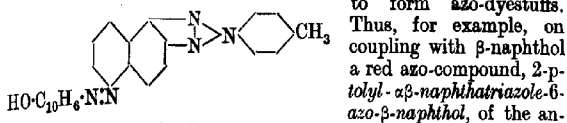
**Constitution of Natural Muscarine.** S. SCILBA (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 518—520).—In order to ascertain if muscarine has the aldehydic structure usually assigned to it, the author treated, with the Angeli-Rimini aldehyde reagent, an extract prepared from *Agaricus muscarius*; no hydroxamic acid was, however, obtained, although the extract showed distinctly the physiological effect of muscarine. To obtain a definite decision on this question, the preparation of a larger quantity of muscarine is contemplated.

T. H. P.

**Preparation of a Series of Substituted  $\alpha$ -Naphthylamines and of the Dyes derived from them.** L. B. HOLLIDAY & Co., LTD., and GILBERT THOMAS MORGAN (Brit. Pat. 191797).—Triazoles derived from  $\alpha$ -naphthylamine are obtained from 5-nitro- $\beta$ -naphthylamine, which is the main product of the dehydration of  $\beta$ -naphthylamine nitrate, by coupling with diazotised *p*-toluidine, whereby 1-*p*-toluenazo-5-nitro- $\beta$ -naphthylamine is obtained, and this compound on oxidation with chromic acid is converted into 6-nitro-2-*p*-tolyl- $\alpha$ - $\beta$ -naphthatriazole, according to the following scheme:



On reduction with stannous chloride, the corresponding 6-amino-1-p-tolyl- $\alpha\beta$ -naphthatriazole is formed. A similar series of reactions may be carried out with 8-nitro- $\beta$ -naphthylamine. The amino-triazoles are capable of conversion into diazo-derivatives which couple readily with phenols, and the more reactive aromatic amines to form azo-dyestuffs.



Thus, for example, on coupling with  $\beta$ -naphthol a red azo-compound, 2-p-tolyl- $\alpha\beta$ -naphthatriazole-6-azo- $\beta$ -naphthol, of the an-

nexed constitution is obtained.

The amino-triazoles can also be coupled with other diazo-compounds, for example, a brownish-red dyestuff, 7-p-nitrobenzene-azo-6-amino-2-p-tolyl- $\alpha\beta$ -naphthatriazole is obtained from the above amino-triazole and diazotised *p*-nitroaniline. The conversion of this substance, by oxidation with chromic acid, into a bis-triazole derivative proves its constitution as an ortho-amino-azo-compound.

G. F. M.

**Adsorption of Uric Acid by Animal Charcoal, Suspensoid Colloids, and Proteins.** K. HARPUDER (*Z. ges. exp. Med.*, 1922, 29, 208—223; from *Chem. Zentr.*, 1923, i, 90—91).—The adsorption of uric acid by animal charcoal follows the ordinary equation,  $y/m = kc^{1/n}$ . The temperature coefficient of adsorption is negative and inappreciable. Adsorption is increased in the presence of hydrochloric acid, decreased in presence of moderate concentrations of alkalis; with higher concentrations of alkalis adsorption is increased. In the presence of large quantities of neutral salts, adsorption is increased. Addition of sodium urate to a colloidal solution of ferric hydroxide produces, first, a marked turbidity and then, with larger quantities of sodium urate, flocculation, the sodium urate being adsorbed by the colloidal ferric hydroxide. Casein in 0.1*N*-alkali solution does not adsorb a neutral urate. In 0.1*N*-acid solution, however, sorption takes place and separation of the urate by ultra-filtration is not possible. The fixation differs in some respects from normal adsorption. The flocculation of casein chloride by neutral salts is facilitated by addition of uric acid. This is due either to a widening of the isoelectric zone or to flocculation before the isoelectric point is reached. Casein in acid solution is flocculated by uric acid directly. 0.373 Millimol. of uric acid flocculate 100 c.c. of 0.75% casein solution in 0.005*N*-hydrochloric acid. The corresponding value for flocculation by sodium chloride is 16.45 millimol., and by sodium sulphate 0.21 millimol. Serum-globulin behaves like casein. The effect of sorption of uric acid on the stability of globulin is less marked than in the case of casein solutions. Albumins show very little sorption of uric acid, which, in consequence, has no effect on their stability. The sorption of uric acid by proteins is held to be governed by intensity of electrical charge and is not a simple adsorption. A purely electrical explanation is, however,

*p*\*

inadequate. Organ extracts from muscle, cartilage, and liver fix uric acid to varying extents, the greatest fixation being shown by liver extract, the least by cartilage extract. G. W. R.

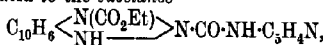
**The Formation of By-products in Diazotisation by Witt's Method.** L. ELION (*Rec. trav. chim.*, 1923, 42, 145-183).—Diazotisation by Witt's method (A., 1909, i, 855) of six substituted anilines, all somewhat basic, showed that the reaction did not in any instance take place wholly in the normal manner. Five of the substances, 3:5-dibromo-4-aminobenzoic acid, 3:5-dibromo-4-aminobenzaldehyde, 3:5-dibromo-4-aminoacetophenone, 3:5-dichloro-4-aminobenzoic acid, 3:5-dibromo-2-aminobenzoic acid, yield, in addition to the anticipated product, a nitro-derivative, whilst the sixth, 3:5-dinitro-4-aminobenzoic acid, furnished a diazonium compound of such instability that it was decomposed by the addition of ice to its solution. The action of the nitric acid on the first four substances is to replace the group in the para-position to the amino-group by a nitro-group in a portion of the product: this takes place when the two ortho-positions with respect to the amino-group are occupied by bromine or chlorine, the groups replaced being carboxyl, acetyl, and the aldehyde group, respectively. In the case of 3:5-dibromo-2-aminobenzoic acid, the bromine atom in the para-position to the amino-group is replaced by the  $\text{NO}_2$ -group, whilst when nitro-groups occupy both ortho-positions, as in 3:5-dinitro-4-aminobenzoic acid, the amino-group is not diazotised to hydrogen, but to hydroxyl, and the carboxyl group in the para-position is left unchanged. In order to study the formation of these by-products, the action of nitric acid on the original amines was investigated and the results showed that in each case in which nitration during diazotisation yields a by-product, the acid yielded a nitrated nitroamine. From 3:5-dibromo-4-aminobenzaldehyde two nitroamines were obtained, one of which contains the aldehydic group unchanged, whilst in the other this is replaced by the nitro-group; the author considers that the latter substance is obtained by secondary nitration. In the case of 3:5-dibromoanthranilic acid, an intramolecular rearrangement of bromine and the nitro-group of the ring takes place subsequently to nitration. With the exception of 3:5-dinitro-4-aminobenzoic acid, a small quantity of a diazonium compound was obtained in each experiment, probably due to the formation of nitrous acid from the nitric acid. The results of direct nitration of the amines suggest that the accessory reaction in diazotisation takes place in such a way that a portion of the original substance is first transformed into nitroamine, which is then diazotised and reduced, thus forming the by-product. The diazotisation of a nitroamine being essentially a reduction, an attempt to bring about this transformation by means of alcohol was made and treatment of 2:6-dibromo-4-nitrophenylnitroamine with alcohol resulted in the formation of 3:5-dibromonitrobenzene. The same change was also effected by Witt's method of diazotisation, which is also accompanied by denitration. The following substances do not

appear to have been described previously: 3:5-dichloro-4-amino-benzoic acid, prepared by chlorination of *p*-aminobenzoic acid, m. p. 291°; 3:5-dinitro-4-nitroaminobenzoic acid, yellow plates containing 1H<sub>2</sub>O, softens at 80°, decomp. 135—136°; 3:5-dinitro-bromobenzene, obtained by diazotising 2:4-dinitro-6-bromoaniline, long, pale yellow plates, m. p. 77°.

H. J. E.

**The Azo-ester Reaction of 3-Aminopyridine.** OTTO DIELS and GEORG BEHNEN (*Ber.*, 1923, 56, [B], 561—566).—It has been shown previously that strongly basic amines react with azodicarboxylic esters to give amides, whereas aliphatic amines generally yield stable additive products of differing types. 3-Aminopyridine is found to behave in the same manner as the strong bases, but in addition to diamides it also yields the ester amides of which representatives have not previously been obtained; they are remarkable for the extraordinary readiness with which the alkyl group of the carbalkoxy-residue suffers replacement.

Ethyl azodicarboxylate reacts vigorously with 3-aminopyridine in alcoholic solution, with the formation of azodicarboxy-di-3-pyridylamide, N<sub>2</sub>(CO·NH·C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>, pale yellow needles, m. p. 164° (decomp.). If the substances are allowed to react at -20°, ethyl azodicarboxy-3-pyridylamidate, C<sub>5</sub>H<sub>4</sub>N·NH·CO·N·N·CO<sub>2</sub>Et, orange-yellow, coarse needles, m. p. 136—137° (decomp.), is obtained; the substance decomposes slowly when preserved, rapidly when treated with dilute acids. The corresponding methyl ester, orange-yellow needles, m. p. 113° (decomp.), is prepared from 3-aminopyridine and methyl azodicarboxylate in methyl-alcoholic solution. It is converted by crystallisation from ethyl alcohol into the ethyl ester, m. p. 136—137°, which is also obtained from methyl azodicarboxylate and 3-aminopyridine in the presence of ethyl alcohol. The ethyl ester is converted by a solution of methylamine in alcohol at -20° into azodicarboxy-3-pyridylmethylamidate, C<sub>5</sub>H<sub>4</sub>N·NH·CO·N·N·CO·NHMe, red crystals, m. p. 137°, and by 5-naphthylamine in the presence of pyridine into the compound, (9)NH<sub>2</sub>C<sub>10</sub>H<sub>6</sub>(2)N(CO<sub>2</sub>Et)·NH·CO·NH·C<sub>5</sub>H<sub>4</sub>N, colourless, lustrous leaflets, m. p. 182° (decomp.) [the hydrochloride, perchlorate, and acetyl derivative, C<sub>21</sub>H<sub>21</sub>O<sub>4</sub>N<sub>5</sub>, m. p. 232° (decomp.), are described]. The compound is oxidised by hydrogen peroxide in the presence of glacial acetic acid to the substance



dark brown needles, decomp. above 250°.

H. W.

**Catalytic Hydrogenation of Alkyl-substituted Pyrroleazodyes.** HANS FISCHER and FRIEDRICH ROTHWEILER (*Ber.*, 1923, 56, [B], 512—519).—Aminopyrroles have previously been very difficultly accessible substances. A number of them are now obtained by the catalytic hydrogenation of pyrroleazo-dyes. Since, however, the behaviour of certain of the compounds is scarcely that which would be expected of substances containing the amino-group, the constitutions are assigned to them with

reserve, since the possibility that an extension of the ring has occurred is not excluded.

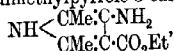
Reduction is effected in alkaline-alcoholic solution in the presence of platinum black. The formation of the hydrazo-compound takes place rapidly, after which further absorption of hydrogen proceeds much more slowly.

Reduction of 2 : 3 : 5-trimethylpyrrole-4-azobenzenesulphonic acid in alkaline solution leads to the production of 4-amino-2 : 3 : 5-trimethylpyrrole,  $\text{NH} \begin{array}{c} \text{CMe} \cdot \text{CMe} \\ \text{CMe} \cdot \text{C} \cdot \text{NH}_2 \end{array}$ , colourless crystals, m. p. 186°

(decomp.), and sodium sulphanilate, which are separated from one another by taking advantage of the ready solubility of the base and the insolubility of the salt in alcohol. The amine gives a hygroscopic *hydrochloride*, prismatic crystals, m. p. 234° (decomp.), and a crystalline *picrate*, m. p. (indefinite) 210–230° (decomp.), after becoming black at 180°. It could not be acetylated, benzoylated, methylated with methyl sulphate, or caused to react with phenylcarbimide.

5-Amino-3-acetyl-2 : 4-dimethylpyrrole,  $\text{NH} \begin{array}{c} \text{C}(\text{NH}_2) \cdot \text{CMe} \\ \text{CMe} = \text{C} \cdot \text{Ac} \end{array}$ , rods, m. p. 223° (decomp.) after darkening and softening at 220°, is obtained similarly from 3-acetyl-2 : 4-dimethylpyrrole-5-azobenzenesulphonic acid; it gives a *picrate*, m. p. 175–190°, after darkening at 175°, according to the manner of heating.

Ethyl 4-amino-2 : 5-dimethylpyrrole-3-carboxylate,



is obtained in the form of the *hydrochloride*, colourless, rectangular leaflets or slender needles, m. p. 212° (decomp.) after previous darkening and softening, by the reduction of 3-carbethoxy-2 : 5-dimethylpyrrole-4-azobenzenesulphonate. The corresponding *picrate* has, according to the mode of heating, m. p. 185–195° after softening at 150°. The *hydrochloride* (as also 4-amino-2 : 3 : 5-trimethylpyrrole) does not appear to lose the amino-group when treated with hydrogen iodide and glacial acetic acid.

3-Acetyl-2 : 4-dimethylpyrrole-5-azobenzenesulphonic acid is obtained in almost quantitative yield by coupling 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylic acid with diazobenzenesulphonic acid, the carboxyl group of the pyrrole being eliminated. In a similar manner, diazotised *p*-nitraniline gives 3-acetyl-2 : 4-dimethylpyrrole-5-*p*-nitroazobenzene, an orange-coloured substance, m. p. 198° (decomp.). 3-Carbethoxy-2 : 4-dimethylpyrrole-5-azobenzene, small, yellow needles, m. p. 127°, is obtained from its components in acetic acid solution; it gives a well-crystallised *picrate*, m. p. 156–158° (decomp.), and *styphnate*, m. p. 163° (decomp.). 2 : 4-Dimethylpyrrole-3-carboxylic acid couples with loss of carbon dioxide with diazobenzenesulphonic acid, *p*-nitrobenzenediazonium chloride, and *p*-dichlorobenzenediazonium chloride, to give crystalline dyes. A loss of the carbethoxy-residue from ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate does not occur even under the energetic action

of diazotised picramide. The aldehyde residue of substituted pyrroles cannot be displaced by the azo-residue; the compounds investigated were ethyl 5-aldehydo-2:4-dimethylpyrrole-3-carboxylate, 3-acetyl-2:4-dimethylpyrrole-5-aldehyde, 2:3:5-trimethylpyrrole-4-aldehyde, ethyl 4-aldehydo-1-*p*-tolyl-2:5-dimethylpyrrole-3-carboxylate, and ethyl 4-hydroxy-5-aldehydo-2-methylpyrrole-3-carboxylate.

H. W.

**Oxidative Fission of Hydrazones and Derivatives of Oxyhydrazine.** MAX BERGMANN, REINHOLD ULPTS, and CHARLOTTE WITTE (*Ber.*, 1923, 56, [B], 679—682).—The isolation of reducing compounds of the sugar group from complex mixtures is frequently effected in the form of their hydrazones from which their regeneration is frequently a matter of difficulty. The possibility of oxidative fission by means of perbenzoic acid has been examined in the cases of simple anils and hydrazones.

Benzophenone is obtained in about 55% yield by the action of perbenzoic acid on an ethereal solution of benzophenonephenylhydrazone. Under similar conditions, benzylideneaniline yields much benzaldehyde and considerable quantities of nitrosobenzene. Oxidation of benzaldehydephenylhydrazone gives benzaldehyde-

phenylhydrazone oxide,  $\text{O} \begin{array}{c} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NHPh} \end{array}$ , pale yellow needles or

prisms, m. p. 201° (corr. decomp.), which is a stable substance. It is decomposed by boiling glacial acetic acid with production of benzaldehyde and phenyl acetate, but the fission is by no means smooth, and large quantities of other substances are produced; a portion is isomerised to benzoylphenylhydrazine, thus showing that the carbon-nitrogen skeleton of the original material is preserved intact in the oxidation product. The oxide is decomposed by phenylhydrazine into dibenzoylphenylhydrazine,  $\text{NHBz} \cdot \text{NBzPh}$ , m. p. 176°, and much benzonitrile, by aniline into *p*-aminodiphenyl, m. p. 54°, and by dimethylaniline into benzamide.

Furfuraldehydephenylhydrazone is oxidised by perbenzoic acid in ethereal solution to furfuraldehydephenylhydrazone oxide,  $\begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad \diagup \quad \diagdown \\ \text{CH} \cdot \text{O} \end{array} \text{C} \cdot \text{CH} \begin{array}{c} \text{N} \cdot \text{NHPh} \\ | \\ \text{O} \end{array}$ , pale yellow or yellowish-brown crystals which appears to be considerably less stable than the corresponding derivative of benzaldehyde.

H. W.

**Colloid Chemical Characteristics of Albumin Fractions. Sensitisation and Protective Action of Hydrophilic Colloids.** J. REITSCHÖTTER (*Kolloid Z.*, 1923, 32, 47).—In opposition to the view held by Pauli, the author has shown that solutions of albumin cannot be submitted to prolonged dialysis without permanent changes taking place in the material. The changes can be detected by the effect of electrolytes on the solutions. Thus an albumin-ferrie hydroxide sol, which has been submitted to electro-dialysis through parchment membranes, is distinctly more sensitive to electrolytes than the pure ferrie hydroxide sol. Albumin-ferrie hydroxide sols are more sensitive to electrolytes than paraglobulin-

ferrous hydroxide sols. The paraglobulin from diphtheria and tetanus serum has a much greater negative charge than the paraglobulin from normal and anti-infection sera. Specific anti-substances have a definite charge which is always more negative than that of paraglobulin from normal sera. J. F. S.

**Some Methods for the Preparation of Ultra-visible Albumin Sols and the Significance of these for Colloid Chemistry and Biology.** A. FODOR (*Kolloid Z.*, 1923, 32, 103—107).—The author describes methods for the preparation of ultra-visible sols of albumin, globulin, and casein. By means of these sols it is shown to be possible to follow the change from the sol to the gel condition. The process consists, in the case of albumin, in the dehydration of the strongly solvated enhydrones of this protein, which are ultramicroscopically invisible, to such an extent that the particles become visible in a dark field illumination. This is achieved by diluting white of egg with ten times its volume of water, adding a crystal of thymol, and keeping for several months in an ice-chest. The solution thereby becomes very opaque, but there is only the smallest amount of coagulation. This is filtered and the filtrate placed in the field of an ultramicroscope which is illuminated by a paraboloid condenser, when relatively large aggregations which do not move markedly are visible. If the solution is now made faintly alkaline with sodium hydroxide, the aggregates are resolved into the primary particles which are in violent motion. If the solution is heated, the field becomes optically empty, but if the solution is kept for a week at 0°, the visible enhydrones are again apparent. J. F. S.

**Nature of the Coagulation of Proteins by Alcohol and other Organic Substances.** W. W. LEFESCHKIN (*Kolloid Z.*, 1923, 32, 100—103).—The nature of the coagulation of albumin by alcohol has been investigated. It is shown that the coagulation by alcohol is similar to the coagulation by heat, and that all factors which affect the heat coagulation have exactly the same effect on coagulation of proteins by alcohol. The addition of alcohol to albumin solutions brings about an acceleration of the velocity of the denaturation, the amount of the acceleration being proportional to the amount of alcohol added. Such a denaturated product would be insoluble in water, as is found to be the case with the albumin coagulum after it has remained in contact with alcohol for a short time. J. F. S.

**Conditions of Reversible and Irreversible Coagulation of Proteins by Salts.** W. W. LEFESCHKIN (*Kolloid Z.*, 1923, 32, 44—46).—Solutions of albumin are coagulated reversibly by salts of the alkali metals, but irreversibly by salts of the alkaline-earth and heavy metals. Further, the coagulation by salts of the alkali metals is irreversible if it takes place in the presence of hydrochloric acid. The varying behaviour is due to the velocity with which the albumin in the various cases is denaturated. The presence of alkaline-earth and heavy metal salts and hydrochloric acid

accelerates the denaturisation in various ways, which are explained in the paper, and so render the coagulation irreversible. J. F. S.

**Relationship of Neutral Salts to Acid Albumins.** SUSUMU MATSUMURA and JOHANN MATULA (*Kolloid Z.*, 1923, 32, 37—42).—After a discussion of the views held by Pauli (A., 1909, i, 618) and Hardy (A., 1906, i, 121) on the mechanism of the reaction between neutral salts and solutions of acid proteins, the authors, who disagree with the views hitherto put forward, describe a number of parallel experiments on the action of hydrochloric acid and sodium chloride on solutions of the chloride of the protein obtained from horse-serum. The serum used had been preserved for several years under toluene and had deposited the whole of the globulin. The dialysed serum was mixed with equal volumes of 0.005N-, 0.01N-, and 0.05N-solutions of hydrochloric acid, respectively, and three solutions thus obtained in which the protein was not completely saturated, saturated, and over-saturated, with acid. These three solutions were treated with equivalent quantities of hydrochloric acid and sodium chloride at the ordinary temperature and at 100°. At the ordinary temperature, the coagulation of the protein takes place with much smaller concentrations of the salt than of the acid, whilst at 100° the same result is observed, but, further, in the case of hydrochloric acid, the amount of precipitation in hot solution is exactly the same as in cold solution, whereas with sodium chloride the amount of precipitate is greater in hot solutions than in cold. A further series of experiments on the electrical conductivity of protein chloride solutions to which hydrochloric acid and sodium chloride, respectively, have been added shows that the salt solution increases the specific conductivity from three to five times as much as the hydrochloric acid. The results indicate that the views put forward previously are inaccurate, and that the action of neutral salts consists in the first place in the formation of a poorly hydrated complex of the protein chloride and the

neutral salt, of the type  $\text{NaCl} \cdot \text{R} \cdot \begin{smallmatrix} \text{NH}_2\text{HCl} \\ \text{CO}_2\text{H} \end{smallmatrix}$ , whereby the electrolytic dissociation of the protein chloride is not markedly affected, but the viscosity is much reduced, and in the second place in the displacement of the ionisation of this complex which brings about the coagulation. J. F. S.

**Precipitation of Serum-albumin by Copper Salts.** SUSUMU MATSUMURA and JOHANN MATULA (*Kolloid Z.*, 1923, 32, 115—118).—The authors have investigated the conditions under which solutions of cupric chloride cause the precipitation of serum-albumin solutions. It is shown that serum and albumin solutions which are entirely free from electrolytes are not precipitated by cupric chloride. Precipitation may be brought about by the presence of large quantities of neutral salts or by the presence of small quantities of alkalis. The nature of the precipitation in the two cases is different. In the first case, the amount of the precipitate increases with the amount of copper chloride added, whilst

in the second case the precipitation is restricted to a definite range of quantities of copper chloride, and with amounts beyond this it passes back into solution. The precipitate in the second case can also be brought back into solution by the addition of neutral salts, whilst in the first case the precipitate is insoluble both in excess of cupric chloride and neutral salt. Copper chloride solutions form positively charged complexes with dialysed albumin, in which the copper chloride is not united to the albumin molecule in the same place as the acid in acid albumins.

J. F. S.

**Reaction of Proteins with the Acids of Soaps and Fats.** I. SUSUMU MATSUMURA (*Kolloid Z.*, 1923, 32, 173—176).—The behaviour of solutions of sodium oleate with dialysed horse-serum has been investigated. It is shown that the whole of the proteins in sera, and also in egg-albumin, give precipitates when treated with soaps of the higher fatty acids. The precipitation is incomplete, but may be made complete by the removal of the free alkali, which retards the formation of the precipitate. The precipitates from dialysed sera which are soluble in sodium chloride solution may be brought permanently into solution by warming at 56°. On the other hand, sera which have been previously warmed at 56° are no longer precipitated by soap solutions. The soap precipitates, which are insoluble in sodium chloride, namely, those of serum-globulin and ovoglobulin, dissolve on warming, but on again cooling they are reprecipitated.

J. F. S.

**The Plant Albumin "Leucosin."** HEINRICH LÜERS and MAX LANDAUER (*Biochem. Z.*, 1922, 133, 598—602).—Leucosin, obtained from barley, and purified by the method of Osborne, shows the following distribution of its nitrogen: ammonia-N, 9.4%; melanin-N, 1.1%; hexone-base-N, 26%; monoamino-N, 63.1%. The results obtained using a shortened method of hydrolysis are also given and show agreement with those given by the longer process.

W. O. K.

**Physical Chemistry of the Globulins. I. Alkali and Alkaline-earth Globulins.** I. Alkali and Alkaline-earth Globulins. MONA ADOLF (*Koll. Chem. Beihefte*, 1923, 17, 1—50).—A physico-chemical investigation of the portion of globulin which is insoluble in water. By electro-dialysis it is found possible to precipitate from human sera and exudations a globulin which is insoluble in water. This material did not change the electrical conductivity of pure water and contained 0.215% of ash and 0.047% of phosphorus. By means of solubility determinations of globulin in alkali and alkaline-earth hydroxide solutions, it is shown that these substances combine with globulin in equivalent quantities, and not in molecular quantities, as hitherto supposed, to form neutral salts. Globulin yields only one form of neutral salt with alkali, a property in which it differs from casein; this salt is not hydrolysed markedly. The power of globulin to combine with bases in an excess of strong alkali hydroxide solution is represented by  $15 \times 10^{-3}$  g. equivalent per g. of albumin, and is proportional to the amount of the latter

substance. The degree of hydrolysis of the albumin salt in aqueous solution is 24%, and the mean acid dissociation constant  $1 \times 10^{-10}$ . Weak bases apparently combine with less globulin, but if referred to isohydric concentrations with more globulin. The salts so formed are all more strongly hydrolysed. The same is true for all proteins hitherto investigated. The viscosity curve for a solution of constant albumin content but increasing alkali hydroxide concentration passes through a maximum both for strong and weak bases. The hydroxide concentration of the viscosity maximum and that at which the maximum combination takes place do not coincide, but the latter quantity corresponds with the maximum electrical conductivity of the protein salt. By measurements of the concentration of hydroxyl-ions and the viscosity, it is shown that the combination of globulin with the base is a time process, and is practically complete after twenty-four hours. The value of  $\lambda_{\infty}$  for the neutral alkali globulinate has been deduced from electrical conductivity measurements, and the following values have been obtained for 25°: sodium globulinate,  $\lambda_{\infty} = 100 \text{ ohms}^{-1}$ ; potassium and ammonium globulinate, 123—124  $\text{ohms}^{-1}$ . From these values the mobility of the globulinate-ion is found to be 50. The valency of the negative globulin is found by the Walden-Ostwald rule to be 4. Three g. of globulin are neutralised by 1 millimol. of alkali hydroxide, and from this the equivalent weight of globulin is calculated to 3000, which indicates a molecular weight of 12,000.

J. F. S.

**Antagonistic Behaviour of Albumin toward Globulin.** G. A. BROSSA (*Kolloid Z.*, 1923, 32, 107—115).—Suspensions of globulin are peptised by negative colloidal solutions of dyes such as Congo-red and benzo-purpurin, and also by positive solutions of colloidal dyes such as night-blue. Of these sols, that obtained by peptising a suspension of globulin with Congo-red has been investigated. The Congo-red-globulin sol is extremely sensitive to electrolytes, and is coagulated by much smaller concentrations of electrolytes than the pure dye sol. The sensitiveness increases with increasing globulin content. The night-blue-globulin sol is also very sensitive. Albumin has a protecting action on the Congo-red-globulin sol, just as it has on the pure Congo-red sol. The antagonistic action of albumin and globulin is also manifested if the albumin or globulin in a serum is increased. A mixture of a Congo-red sol and a serum rich in globulin is much more sensitive than a mixture of a Congo-red sol and a serum rich in albumin. From this it is deduced that generally a serum which is richer in globulin than in albumin is more sensitive to electrolytes than one which is richer in albumin than in globulin for the same total protein content. This rule is found to be true when the globulin rich horse-serum is compared with the globulin poor rabbit-serum, and when pathological human-serum is compared with normal human-serum. From Kruyt's experiments (*ibid.*, 1922, 31, 338), it follows that colloidal solutions of negative dyes such as alkali-blue, water-blue, Chicago-blue, as well as the positive dye night-

blue, are rendered more sensitive by the addition of tannin. Since in this case the increase in sensitiveness cannot be occasioned by the discharge of the colloid particles by the added substance, it is very questionable whether the discharge of the colloid particles causes the increase of sensitiveness in the present case. J. F. S.

**The Hydrolysis of Edestin with Sulphuric Acid.** J. S. JÄTTISCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 105–108).—Edestin is hydrolysed with sulphuric acid of various concentrations, varying the temperatures and the times of reaction. The reaction mixture is in each case neutralised with sodium hydroxide, and Fassbender's reagent added. The precipitate is analysed for nitrogen by Kjeldahl's method, and the amount of nitrogen found serves as a measure of the amount of unhydrolysed albumin. Increase in temperature and in  $H^+$ -concentration have an accelerating effect on the hydrolysis, the influence of the former being more marked. R. T.

**Identity of Hordein and Bynin.** HEINRICH LÜERS (*Biochem. Z.*, 1922, 133, 603–604; cf. A., 1919, i, 603).—The equation given in the previous paper for the calculation of the histidine-nitrogen is incorrect. The recalculated values are now given. W. O. K.

**The Products of Prolonged Tryptic Digestion of Casein.** SIGMUND FRÄNKEL and KATHARINE GALLIA (*Biochem. Z.*, 1922, 134, 308–321).—Casein was digested with pancreatin for sixty days at  $37^\circ$ . A hot-water extract of the precipitate gave *d*-tyrosine anhydride and the mercuric sulphate precipitate of the filtrate contained tryptophan anhydride. On removal of mercury the filtrate was precipitated with phosphotungstic acid, and the filtrate from this on removal of foreign ions gave successive crops of crystals. The first crop was identified as *d*-tyrosine; it had a higher rotation,  $[\alpha]_D + 17.9$ , than any previously recorded value. The second and third crops consisted of *dl*-valin, and the fourth crop of *d*-valin. The formation of *d*-tyrosine is ascribed to a Walden inversion produced by an enzyme *Waldenase*. H. K.

**The Oxygen-dissociation Curve of Blood, and its Thermodynamical Basis.** W. E. L. BROWN and A. V. HILL (*Proc. Roy. Soc.*, 1923, [B], 94, 297–334).—On the assumption that the combination of oxygen or carbon monoxide with hæmoglobin in blood (as distinct from dialysed hæmoglobin) is a reversible chemical reaction of the following type:  $H(Hb)_n + nO_2 \rightleftharpoons H(HbO_2)_n$  (cf. A., 1910, i, 288; A., 1922, i, 193), the authors have calculated, with the aid of the van't Hoff isochore, that the heat of reaction,  $q$ , of 1 mol. of hæmoglobin,  $H(Hb)_n$ , with  $n$  mols. of oxygen at constant volume is 19,000 cal. in the presence of carbon dioxide and 30,500 cal. in its absence. Direct estimations of the heat  $Q$  evolved when 1 mol. of oxygen combines, at constant volume, with hæmoglobin in blood have given a value of 14,400 cal. in the absence of carbon dioxide. The ratio  $q/Q$  is obviously equal to  $n$ ; hence  $n = 305/144 = 2.1$  approximately. This agrees with the value

obtained independently from the shape of the dissociation curve and from other data, and is consequently regarded as confirmation of the theory of the reversible chemical combination of oxygen with hæmoglobin. The difference in the value of  $q$  in the presence and absence of carbon dioxide is due to the absorption of heat which occurs when carbon dioxide is expelled from its combination with base by the stronger acid,  $H(HbO_2)_n$ . Calculations of the acid dissociation constants of unsaturated hæmoglobin and carboxy-hæmoglobin [ $\overline{HHb}_n$  and  $H(\overline{HbCO})_n$ ] have given values of  $7.5 \times 10^{-9}$  and  $5 \times 10^{-7}$ , respectively.

E. S.

**Tryptophan and Tyrosine Content of Hæmoglobin and other Blood Proteins.** U. KIYOTAKI (*Biochem. Z.*, 1922, 134, 322—335).—Globin prepared in a variety of ways contains 3.6% of tryptophan when estimated colorimetrically by Fürth and Lieben's application of the Voisenet reaction. In agreement with this, the amount of melanoidin formed by acid hydrolysis was 3.3%. The tryptophan is only liberated with difficulty from hæmoglobin, 18% being set free after three weeks' tryptic digestion with a highly active trypsin. The tyrosine content of globin was found to be between 3.5% and 4%, corresponding with one molecule of tyrosine for every molecule of tryptophan. In serum-albumin 5 mols. of tyrosine and in serum-globulin 2 mols. of tyrosine were found for every tryptophan molecule.

H. K.

**Hydrolysis of Yeast-nucleic Acid with Dilute Alkali at Room Temperature (Conditions of Steudel and Peiser).** P. A. LEVENE (*J. Biol. Chem.*, 1923, 55, 9—13).—Contrary to the results obtained by Steudel and Peiser (*A.*, 1922, i, 782), it has been found that, under the conditions used by these authors, the removal of guanylic acid from yeast-nucleic acid is incomplete. Moreover, the formation of the remaining three nucleotides occurs simultaneously with that of guanylic acid.

E. S.

**Determination of the Isoelectric Point of Gelatin. A Criticism of Patten and Kellems's Method.** THOMAS SLATER PRICE (*T.*, 1923, 123, 410—412).

**Keratinisation.** UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 133, 476—486).—Analyses have been carried out of the amino-acids of keratin from hair, nails, and from corns (of the foot). The cystine content, particularly, varies according to the source of the keratin.

W. O. K.

**The Origin of the Humin Formed by the Acid Hydrolysis of Proteins. VII. Hydrolysis in the Presence of Ketones.** ROSS AIKEN GORTNER and EARL R. NORRIS (*J. Amer. Chem. Soc.*, 1923, 45, 550—553; cf. *A.*, 1915, i, 726; 1916, i, 681; 1918, i, 84; 1920, i, 400, 450).—Fibrin was hydrolysed alone and in the presence of acetone and acetophenone, and the distribution of the nitrogen among the products was studied. Apparently the presence of ketones does not alter the nitrogen distribution as measured by

Van Slyke's method. Acid-insoluble humin formed during a protein hydrolysis does not apparently come from the interaction of a ketone and tryptophan. W. G.

**The Specificity of Enzymes.** RICHARD WILLSTÄTTER and RICHARD KUHN. I. The Theory of Time Value Quotients. (*Z. physiol. Chem.*, 1923, 125, 1—27).—A general discussion is given of the kinetics of enzyme action with special reference to the possible modes of action of accelerators and inhibitors. The question of the identity of enzymes in different preparations is considered, and the related question of the specificity of enzymes. A distinction is drawn between relative and absolute specificity, the first being a quantitative and the second a qualitative difference in their modes of attack on substrates. W. O. K.

**Units of Enzymes.** RICHARD WILLSTÄTTER and RICHARD KUHN (*Ber.*, 1923, 56, [B], 509—512).—A system of nomenclature is proposed in which the figures are directly proportional to the quantities and enzymatic concentrations of the preparations. The lipase unit is the quantity of enzyme which causes the fission of 2.5 g. of olive oil to the extent of 24% during one hour. The amylase unit is one hundred times the quantity of enzyme of  $k=0.01$  and the peroxydase unit is equal to 1 g. of the purpurogallin number I. The lipase and amylase values are the number of units in 1 cg. The saccharase unit (*SE*) is the amount of enzyme in 50 mg. of material containing invertin of the time value 1 in accordance with the definition of O'Sullivan and Thompson. The purity of an invertin preparation (*SW*) is expressed by the reciprocal of the time-value, and thus denotes the number of saccharase units in 50 mg. substance. The relationship of the saccharase value to the inverting power as defined by von Euler and Svanberg is expressed by the equation:  $SW = If/46.176$ . The expressions for quantity and concentration are not universally applicable for invertin and other enzymes, since their behaviour towards sucrose is considerably influenced by the varying amounts of foreign matter with which they are associated. For the strict comparison of saccharase preparations of different origin the dissociation constants should be appended to the *SW* and *SE*. Invertins of different affinities are compared by calculation of the units measured in the usual manner, which is sufficiently exact for preparative work to an invertin of the medium affinity constant=50 ( $k=0.020$ ). The "reduced saccharase unit" is calculated according to the formula  $SE_{red} = S.E.(n+k/n+0.02)$ , in which  $n$  is the normality of the sucrose solution in which the constants of the reaction are estimated. H. W.

**The Nomenclature of Autolytic Enzymes.** K. G. DERNEY (*Biochem. Z.*, 1922, 133, 432—433).—The author proposes to classify the proteolytic enzymes of plant or animal cells as primary proteases (pepsinases), secondary proteases (trypsinases), and tertiary proteases (ereptases), which act on protein in acid solution, on denatured protein and peptone in alkaline and neutral solution, and on peptides in alkaline solution, respectively. W. O. K.

**A Comparison between the Chemical and Physiological Characteristics of Pepsin and Rennin.** FREDERIC FENGER (*J. Amer. Chem. Soc.*, 1923, 45, 249—255).—Pepsin and rennin are proteins possessing widely different properties. Pepsin is coagulated by heat and is colloidal in nature, but rennin is a decomposition product of protein of the acid-albumin type, and is not precipitated on boiling. Pepsin may be dialysed without loss, but rennin readily diffuses through a parchment membrane. Proteolytic or peptic activity does not seem to be a part of the true physiological characteristics of the milk-curdling enzyme. Both enzymes are present in the stomach of the suckling calf, but in that of the adult hog only pepsin was found. W. G.

**The Influence of Starch on Peptic Digestion.** ANTON FISCHER (*Biochem. Z.*, 1922, 134, 360—362).—Contrary to statements in physiological literature, the addition of starch has no inhibiting action on the digestive action of pepsin. H. K.

**The Specificity of Enzymes. II. Saccharase and Raffinase Activity of Invertase.** RICHARD WILLSTÄTER and RICHARD KUHN (*Z. physiol. Chem.*, 1923, 125, 28—92).—The influence of hydrogen-ion concentration on the hydrolysis of sucrose by invertase is apparently due to its action on the rate of decomposition of the compound of enzyme and substrate. This is shown by the fact that if the affinity constant  $K = \frac{[\text{Enzyme}][\text{Substrate}]}{[\text{Enzyme-Substrate}]}$  be determined from measurements of the kinetics of the inversion,  $K$  is independent of the hydrogen-ion concentration. The affinity constant  $K$  does not vary with the degree of purity of the enzyme preparation, but is different in preparations made from yeasts of different sources, varying in the preparations tested from 0.016 to 0.040. If to one preparation there is added the solution obtained by heating another preparation so as to inactivate it, filtering from any coagulated protein, the affinity constant of this first preparation may be altered, in all the combinations tried a value of  $K = 0.030$  being obtained.

Similar variations in the affinity constant of invertase for raffinose depending on the origin of the yeast have been found, and a comparison of the effects of invertase on raffinose and on sucrose leads to the conclusion that ratio of the affinity constants of the different preparations is constant, and likewise the ratio of the molar quantities of the two sugars hydrolysed by a given amount of invertase under optimum conditions, if extrapolated to the value for infinite quantities of substrate. There appear to be strong indications that the saccharase and raffinase present in invertase are identical. W. O. K.

**The Preparation of Highly Active Invertin and its Sulphur Content.** H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, 56, [B], 453—455).—The term invertin is applied to the natural group of enzymes obtained from yeast-cells or similar materials which causes the enzymatic inversion of sucrose and contains saccharase

as its main component. Highly active specimens ( $I_f=182$ ) are readily obtained from "aged" autolysed yeast-juice by fractional precipitation and dialysis combined with adsorption by aluminium hydroxide and elution with potassium arsenate solution.

A specimen which has the value  $I_f=182$  contains 0.38% of sulphur, corresponding with 0.48% S in a specimen having  $I_f=230$ . If this sulphur content is due to the presence of one atom of sulphur in the saccharase molecule, the combining weight of the latter is 6700, a value which is somewhat greater, but of the same order of magnitude as that derived from the analysis of silver saccharase.

H. W.

**Saccharase.** H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, 56, [B], 446—452).—The preparation of highly active saccharase from autolysed yeast-juice is effected by a combination of the methods of fractional precipitation and dialysis with those of adsorption by aluminium hydroxide and elution with potassium arsenate. The parallelism between phosphorus content and activity ceases when the value of  $I_f$  exceeds about 100. The phosphorus content of the most active specimens ( $I_f=210$  at 18°) is 0.15%, and is therefore considerably higher than the lowest value recorded by Willstätter (0.03—0.006%), whose specimens were obtained from "aged" autolysed juice with the aid of lead acetate (cf. Willstätter and Racke, A., 1922, i, 598; Willstätter, Graser, and Kuhn, A., 1922, i, 1200; Willstätter and Wassermann, this vol., i, 69). Analysis of the most highly active specimens gives ash=4.0%, C=45.58%, H=6.70%, N=12.7%, P=0.15%, As<0.1%.

The preparation of the silver compound of saccharase (von Euler and Josephson, A., 1922, i, 1076) has been repeated with highly active saccharase; it contains about 2% of silver, thus indicating a minimum molecular weight of about 5400 for the enzyme.

The methods of indicating the activity of saccharase preparations are described. The conversion of the inverting capacity ( $I_f$ ) to the time values of O'Sullivan and Thompson (T., 1899, 57, 834) is effected by multiplication by the factor 58.6. H. W.

**The Action of Quinine and Quinine Derivatives on Stomach Lipase.** P. RONA and M. TAKATA (*Biochem. Z.*, 1922, 134, 118—130).—Stomach lipase (from the small stomach of a dog by Pavlov's method) is inhibited by quinine and its derivatives, quinidine, optoquin, eucupin, and vuzin, to an extent corresponding with their property of lowering the surface tension as measured by the drop number. The degree of inhibition depends on the hydrogen-ion concentration of the solution and therefore on the degree of dissociation of the quinine salt, and on the quinine concentration, but not on the concentration of the ferment. The quinine concentration-inhibition curve is an adsorption isotherm, the logarithm of the quinine concentration being proportional to the logarithm of the inhibition. H. K.

**The Action of Quinine and of Atoxyl on Pancreatic Lipase.** P. RONA and R. PAVLOVIĆ (*Biochem. Z.*, 1922, 134, 108—117).—The action of pancreatic lipase is strongly inhibited by quinine, but not by atoxyl. Liver lipase, however, is very sensitive to atoxyl. If the logarithms of the quinine concentration be plotted against the logarithms of the degree of inhibition, a straight line is obtained. Sodium fluoride inhibits the action of pancreatic lipase slightly, that of liver and serum lipase strongly. H. K.

**Pancreatic Enzymes. I. Determination of Pancreatic Fat Hydrolysis.** RICHARD WILLSTÄTTER, ERNST WALDSCHMIDT-LEITZ, and FRIEDRICH MEMMEN (*Z. physiol. Chem.*, 1923, 125, 13—131).—The activity of the lipase of the pancreas, unlike that of invertase, is dependent on its state of dispersion and on the colloidal material present in the solution containing it. In the case of invertase, these factors do not affect the activity, but only the stability of the preparations (cf. A., 1922, i, 1200). The activity of lipase is, of course, also dependent on the hydrogen-ion concentration, and so, as in the hydrolysis of triolein, acid is being constantly produced and the rate of the reaction thus being changed, direct measurement of the activity is not possible. The estimation of the activity may be carried out in three ways, (1) in an acid medium, of constant  $P_H$  of 4.7, this being approximately the  $P_H$  on adding oleic acid to water; (2) in an alkaline medium, the reaction being kept constant by the presence of a large amount of buffer solution, which, however, interferes to some extent with the activity; (3) in a medium alkaline at first, which, however, is allowed to become acid as the reaction proceeds. In the last case, the results are calculated from the observed course of the hydrolysis. As the activity of the enzyme solution depends on the other substances present, it is necessary, in order to obtain comparable results, to add activators, a suitable combination being calcium chloride and albumin.

If the activity of lipase adsorbed by various adsorbing surfaces be measured, it is found that the adsorbents fall into two groups, those which at most only slightly diminish the activity of the lipase (e.g., kaolin or aluminium hydroxide), and those which render the adsorbed lipase practically inactive (tristearin and cholesterol). It is suggested that, in the latter cases, the specifically active groups of the lipase molecule are held firmly by the surface, whilst in the former cases the active groups are free, and adsorption depends on other groups of the molecule. W. O. K.

**Pancreatic Enzymes. II. Pancreatic Lipase.** RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Z. physiol. Chem.*, 1923, 125, 132—198).—Pancreatic lipase, as obtained by extraction of the pancreatic glands by glycerol, is mixed with amylase and trypsin. Lipase shows both acid and basic properties, and is adsorbed by aluminium hydroxide and by kaolin. Pancreatic amylase and trypsin, on the other hand, have no marked acid properties, and when in a pure condition they are not adsorbed by aluminium hydroxide. However, when mixed with lipase they

are adsorbed to some extent, but at most a very small amount of these is washed out by ammonium phosphate, which removes the lipase. On repeating the process, lipase is obtained free from amylase and trypsin. Amylase and trypsin may be separated by utilizing the fact that the basic properties of trypsin are more marked, and that it is preferentially adsorbed from acid solution by kaolin.

Further purification of the lipase is effected by adsorbing on kaolin, and extracting with alkali phosphate. This may be followed by adsorption on cholesterol or tristearin, which are particularly selective in their adsorptive action. Very full details of these processes are given in the original paper. Only traces of the colour reactions of any known group of organic compounds are given by the purified lipase, which has been obtained in a concentration three hundred times that in dried pancreas.

W. O. K.

**Ferments and Light. I. Diastase. I. LUDWIG PINCUSSEN** (*Biochem. Z.*, 1923, **134**, 459—469).—Diastase, independently of dilution, loses its activity on exposure to ultra-violet rays in a quartz tube, but not in sunlight. The destruction by light is greatest at a  $P_H$  of 4.6, which is the optimum reaction for diastatic activity, and is least between  $P_H$  7 and 7.4. The presence of salt influences the rate of destruction by ultra-violet light, iodide increasing it. Sugars are without effect in ultra-violet light, although in presence of dextrose even sunlight is slightly effective. The effect of ultra-violet light is inhibited by glycine and starch. Temperature has apparently little effect.

W. O. K.

**The Action of Iodine on Diastase. L. BERCZELLER and J. FREUD** (*Biochem. Z.*, 1922, **133**, 493—501).—The action of saliva diastase is decreased by iodine, but it is not completely inactivated. Starch protects the diastase against the action of iodine. In the same way, the hydrolysis of starch by mineral acids is also inhibited by iodine.

W. O. K.

**The Action of Calcium on the Clotting of Milk by Rennin. P. RONA and E. GABBE** (*Biochem. Z.*, 1922, **134**, 39—75).—An extensive series of experiments was carried out on the influence of calcium on the clotting of milk under specified conditions as regards dilution, time, temperature, and hydrogen-ion concentration. The course of fermentation was followed by observing the temperature at which samples removed at intervals were clotted by heat. If calcium chloride is added at the beginning of the fermentation, the time which elapses before clotting is the longer the higher the calcium content. Small concentrations of calcium stimulate the ferment action, but large concentrations inhibit it. If, however, the calcium chloride is added after the fermentation has been in progress some time, the period before clotting is prolonged. The conversion of caseinogen into casein is only complete at hydrogen-ion concentrations between  $P_H$  6.0 and 6.4.

H. K.

**Experiments on Liver Catalase.** PETER RONA and ARISTIDA DAMBOVICBANU (*Biochem. Z.*, 1922, 134, 20—38).—A series of experiments carried out on the catalase of calf's liver showed that the activity is not affected by the particular buffer mixture used, and that the optimum activity is exhibited over a broad range of  $P_H$  round about 7 and is only inhibited at  $P_H$  11. If the ferment is in excess of the hydrogen peroxide, the reaction is unimolecular, but if the ferment is only sufficient to decompose 65 to 80% of the hydrogen peroxide, the reaction is bimolecular. Chloridion inhibits the fermentation, but a 0.0005 molar sodium hydrogen carbonate solution is sufficient to inhibit the action of a 0.154 molar sodium chloride solution. If, however, the ferment is in large excess over the peroxide, the inhibiting action of chloridion is not so noticeable.

H. K.

**Ferments and Light. II. Urease.** I. LUDWIG PINCUSSEN and NAOSABURO KATO (*Biochem. Z.*, 1923, 134, 470—475).—Urease gradually loses its activity on exposure to sunlight or to ultra-violet light, most rapidly apparently at the reaction optimum for the activity of the urease.

W. O. K.

**Synthesis of Carbamide with the Enzyme Urease.** EDWARD MACK and DONALD S. VILLARS (*J. Amer. Chem. Soc.*, 1923, 45, 501—505).—It is shown that, when concentrated solutions of ammonium carbonate and carbamate are used, the enzyme urease acts reversibly and increases the velocity of formation of carbamide, hastening the attainment of the equilibrium. A 1% solution of the enzyme will bring about equilibrium in a 10*N*-ammonium carbonate-carbamate solution, containing about equal amounts of each salt, in about ten hours at 55°, whereas with a 0.1% solution of the enzyme the reaction is only about one-third complete in ninety-eight hours and without any enzyme equilibrium would be attained only after about six hundred days at 55°.

W. G.

**The Action of Urease in the Decomposition of Carbamide.** EDWARD MACK and DONALD S. VILLARS (*J. Amer. Chem. Soc.*, 1923, 45, 505—510).—Experimental evidence is given to show that the transformation of ammonium cyanate into carbamide is not catalysed by the enzyme urease, but rather that the enzyme is slowly poisoned by the cyanate. When carbamide is hydrolysed, in the presence of urease, forming ammonium carbamate, which changes into the carbonate, there is simultaneous formation of ammonium cyanate from the carbamide. When considering the different stages possible in the transformation of carbamide into ammonium carbonate, it is shown by a process of elimination that the particular stage catalysed by the urease is the transformation of carbamide into ammonium carbamate.

W. G.

**The Urease of Fungi.** A. GORIS and P. COSTY (*Compt. rend.*, 1923, 176, 412—414).—A study of the urease of the higher fungi and in particular of *Boletus edulis*, Bull. This urease is not very sensitive to heat, only being destroyed at 76°. The optimum temperature is 30—38°. It is very sensitive to mineral and organic

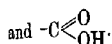
acids. Of the organic acids studied, tartaric acid is the most injurious and acetic acid the least. The enzyme is less sensitive to alkalis, and it is able to resist a concentration of ammonium carbonate ten times as great as that of sodium carbonate, which destroys it. Of the neutral salts studied, those of calcium exert the greatest retarding action, and then, in descending order, those of sodium, potassium, ammonium, and magnesium. In general, antiseptics act very energetically on this enzyme. W. G.

**Isomorphism in the Organo-metallic Series. V. Saturated Derivatives of Quinquevalent Metals and Metalloids.** P. PASCAL (*Bull. Soc. chim.*, 1923, [iv], 33, 170—180).—A study was made of the temperatures of fusion and solidification of binary mixtures of oxides and sulphides of triphenylphosphine, triphenylarsine, and triphenylstibine, and the temperatures of the commencement and completion of solidification of the mixed substances in varying proportions are given in tables and curves. The results may be conveniently summarised by designating the types of binary mixtures obtained, arranged in the order of decreasing crystalline analogy, by (1), (2), (3), (4), where (1) is the formation of mixed crystals in all proportions, the curve being spindle-shaped; (2) mixed crystals in all proportions, curve with a minimum; (3) no mixed crystals, curve with a transition point, and (4) no mixed crystals, curve showing a eutectic point, and the following indicates the type to which each binary mixture belongs:  $(\text{PPh}_3\text{O}, \text{AsPh}_3\text{O})=1$ ,  $(\text{PPh}_3\text{S}, \text{AsPh}_3\text{S})=2$ ,  $(\text{PPh}_3\text{O}, \text{AsPh}_3\text{S})=4$ ,  $(\text{PPh}_3\text{S}, \text{SbPh}_3\text{S})=2$ ,  $(\text{PPh}_3\text{O}, \text{SbPh}_3\text{S})=4$ ,  $(\text{AsPh}_3\text{O}, \text{AsPh}_3\text{S})=2$ ,  $(\text{PPh}_3\text{S}, \text{PPh}_3\text{O})=2$ ,  $(\text{PPh}_3\text{S}, \text{AsPh}_3\text{O})=4$ ,  $(\text{AsPh}_3\text{O}, \text{SbPh}_3\text{S})=4$ ,  $(\text{AsPh}_3\text{S}, \text{SbPh}_3\text{S})=2$ . It appears, therefore, that if in a pair of organo-metallic compounds the asymmetry of the central atoms is increased by the addition of oxygen in one and of sulphur in the other, the tendency to isodimorphism is increased. If, on the other hand, the central atoms are saturated by the same element—oxygen or sulphur—the tendency to isomorphism is increased. Binary mixtures in which the phenyl group of the phosphines was replaced by the  $-\text{OPh}$ ,  $-\text{SPh}$ , and  $\text{C}_2\text{H}_5-$  groups, were also examined. The same relations of isomorphism were found to exist between the phosphate and thiophosphate as between the phosphine oxide and sulphide, but isodimorphism occurs when aliphatic groups are introduced into one of the constituents of the binary mixture, or when phenyl and oxyphenyl derivatives are mixed. G. F. M.

**Substitution Factors of the Affinity Constants in the Group of the Arsinic Acids.** RICHARD LORENZ and ELISABETH BREHMER (*Ber.*, 1923, 56, [B], 742—750).—The dissociation constants of a large number of substituted phenylarsinic acids have been measured, and from the results the authors have constructed a table of factors for the mathematical expression of the influence of various groups in differing positions in the molecule. The following data are recorded, Wegscheider's factors for the carboxylic acids being placed within brackets: *o*-Nitro, 1.41, 1.51\* (103); *m*-nitro, 5.0, 5.5 (5.75); *p*-nitro, 5.3 (6.6); *o*-hydroxy,

0.42 (17.0); *m*-hydroxy, about 1.45\* (1.45); *p*-hydroxy, 0.55 (0.48); *o*-methyl, 2.4\* (2.00); *m*-methyl, 0.85\* (0.86). The factors marked with an asterisk are based on experiments with acids containing an amino-group. The dissociation constant of phenylarsinic acid is 0.027. In general, the two tables exhibit a close similarity, the marked divergences occurring in cases where the substituent is in the ortho-position to the carboxyl or arsenic group.

The conductivity of a substituted arsenic acid depends therefore on that of the parent acid, on the nature and position of the substituent (the effect is the same on the arsenic as on the carboxyl group provided that the groups are not too close to one another, in which case an additional factor enters), and on the immediate mutual action between acid radicle and substituent. The latter action is more marked in the arsenic than in the carboxylic series. In the latter, an increasing influence of the substituent is invariably observed as it more closely approaches the carboxyl group; the mutual action of the groups is not sufficiently great to overpower the effect of propinquity. The anomalies in the conductivity of di-ortho-substituted carboxylic acids, however, show that such mutual influence does exist. Possibly it is more marked in the arsenic acids by reason of the relatively greater arsenic residue,  $\text{O:As} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$



H. W.

**The Crystalline Form of some Organic Derivatives of Arsenic.** G. GILTA (*Bull. Soc. chim. Belg.*, 1923, **32**, 19–26).—A detailed crystallographic examination of *p*-aminophenylarsinic acid and of the pentahydrate of its sodium salt (cf. A., 1922, i, 961). Acid: monoclinic [ $a:b:c=1.393499:1:1.162276$ ,  $\beta=101^\circ 20'$ ]. The effect of conditions on the predominant forms (including a twin) is discussed. Sodium salt pentahydrate: monoclinic [ $a:b:c=2.181215:1:0.960163$ ,  $\beta=91^\circ 4'$ ]; measurements are also given of a crossed twin. Tri- and di-hydrates of the sodium salt have been obtained but not measured.

E. E. T.

**Crystalline Form of Atoxyl [Sodium *p*-Aminophenylarsinate] and its Characterisation using the Microscope.** J. MÉLON (*Bull. Acad. roy. Belg.*, 1922, [v], **8**, 150–158).—A detailed crystallographic examination of atoxyl ( $+4\text{H}_2\text{O}$ ): monoclinic,  $a:b:c=0.986590:1:1.251538$ ,  $\beta=82^\circ 5'$  (cf. A., 1922, i, 961, and preceding abstract).

E. E. T.

**Arsenated Benzophenone and its Derivatives. II.** W. LEE LEWIS and H. C. CHEERTHAM (*J. Amer. Chem. Soc.*, 1923, **45**, 510–515; cf. A., 1922, i, 187).—By means of the Friedel and Crafts' reaction dichloro-*o*-arsinobenzoyl chloride has been condensed with a number of aromatic hydrocarbons and aromatic ethers to give new benzophenone arsenic acids. These compounds are easily and quantitatively reduced in acetic acid solution by concentrated hydrobromic or hydriodic acids to derivatives of arsenious oxide. In some cases, the reaction goes further, coloured crystalline

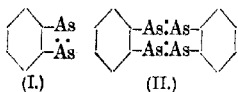
dibromo- or di-iodo-arsines being formed. The latter are easily converted again into the oxide by hydrolysis with dilute sodium carbonate. If the arsenic acids or, better, the arsenious oxides are heated under a reflux condenser with phosphorous acid in alcoholic solution, arseno-derivatives are obtained. The following new compounds are described: *Dichloro-o-arsinobenzoyl chloride*,  $\text{AsCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ , *benzophenone-2'-arsinic acid*,  $\text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , *4-methylbenzophenone-2'-arsinic acid*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , *4-methoxybenzophenone-2'-arsinic acid*,  $\text{C}_6\text{H}_4(\text{OMe}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , *4-phenoxybenzophenone-2'-arsinic acid*,  $\text{C}_6\text{H}_4(\text{OPh}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , *4:4'-dibenzoylarsenobenzene*,  $2:2'$ -di-*p*-anisoylarsenobenzene,  $4:4'$ -diethoxybenzoyl- $2:2'$ -arsenobenzene,  $4$ -methoxybenzophenone- $2'$ -dibromoarsine,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsBr}_2$ , m. p.  $161^\circ$ ,  $4$ -ethoxybenzophenone- $2'$ -dibromoarsine, m. p.  $152^\circ$ ,  $4$ -methoxybenzophenone- $2'$ -arsenious acid,  $4$ -methoxybenzophenone- $2'$ -dichloroarsine, m. p.  $148^\circ$ ,  $4$ -methoxybenzophenone- $2'$ -di-iodoarsine, m. p.  $137^\circ$ ,  $4$ -ethoxybenzophenone- $2'$ -di-iodoarsine, m. p.  $151^\circ$ ,  $4$ -methoxybenzophenone- $4'$ -dichloroarsine, m. p.  $152^\circ$ ,  $4$ -methoxybenzophenone- $4'$ -dibromoarsine, m. p.  $136^\circ$ ,  $4$ -methoxybenzophenone- $4'$ -di-iodoarsine, m. p.  $105^\circ$ ,  $4$ -methoxybenzophenone- $4'$ -arsinoacetic acid. *Acetophenone-p-arsinic acid* is obtained when *p*-aminoacetophenone is diazotised and the product is treated with a solution of sodium arsenite. W. G.

**Silver Salvarsan.** WILLIAM HERBERT GRAY (T., 1923, 123, 635—642).

#### Aromatic Diarsinic Acids and their Reduction Products.

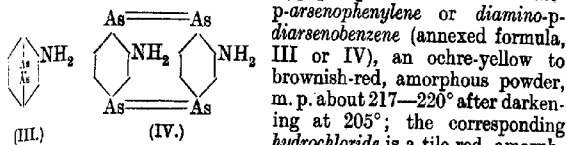
II. H. LIEB and O. WINTERSTEINER (Ber., 1923, 56, [B], 425—433).—In a previous communication (Lieb, A., 1921, i, 696), it has been shown that *m*- and *p*-phenylenediarsinic acids are reducible by phosphorous acid in sealed tubes at an elevated temperature to yellow, amorphous substances of the composition  $(\text{C}_6\text{H}_4\text{As}_2)_n$ , the molecular weight of which could not be determined on account of their insolubility in all suitable media. It is now found that the reduction can be more conveniently effected in open vessels by hypophosphorous acid. With the object of obtaining sufficiently soluble compounds, the observations have been extended to a number of derivatives, none of which, however, fulfils the required conditions.

*o*-Phenylenediarsinic acid is converted by hypophosphorous acid (d 1.28) into *o*-arsenophenylene or *o*-diarsenobenzene (annexed formulæ I or II), an egg-yellow, amorphous precipitate.



*o*-Nitroaniline is transformed by an equimolecular quantity of arsenic acid at  $210^\circ$  into a mixture of 3-nitro-4-aminophenylarsinic acid (cf. Mameli, A., 1909, i, 980; Berthelm, A., 1911, i, 1055) and di-3-nitro-4-aminophenylarsinic acid (Fargher, T., 1919, 115, 982). The former acid is converted by diazotisation and treatment with sodium arsenite in the presence of a little ammoniacal copper sulphate solution into 2(3)-nitrophenylene-*p*-diarsinic acid, colour-

less, pointed prisms, decomp.  $239-243^{\circ}$ ; the corresponding zinc and sodium salts are described. The acid is reduced by sodium amalgam in the presence of methyl alcohol to 2(3)-amino-p-phenylenediarsinic acid, long, oblique prisms which can be obtained only with difficulty in the colourless condition; the zinc salt is described. The nitro-acid is transformed by hypophosphorous acid into amino-



p-arsenophenylene or diamino-p-diarsenobenzene (annexed formula, III or IV), an ochre-yellow to brownish-red, amorphous powder, m. p. about  $217-220^{\circ}$  after darkening at  $205^{\circ}$ ; the corresponding hydrochloride is a tile-red, amorphous precipitate which decomposes gradually when heated above  $220^{\circ}$ . 2(3)-Methyl-p-phenylenediarsinic acid is prepared by the action of sodium arsenite on a diazotised solution of 4-amino-3-methylphenylarsinic acid; it crystallises in colourless leaflets which darken at  $280^{\circ}$  and decompose at  $330^{\circ}$ ; its properties are considerably affected by the presence of small amounts of organic and inorganic impurities, from which it is conveniently freed through its magnesium salt, a white, amorphous precipitate; the sodium salt ( $+9H_2O$ ) and the amorphous barium salt,  $C_7H_5O_6As_2Ba$ , are also described. The acid is reduced by hydrogen sulphide to the sulphide,  $C_6H_3Me(AsS)_2$ , a pale yellow, amorphous precipitate, and by phosphorous acid at  $190^{\circ}$  to methyl-p-arsenophenylene or dimethyl-p-diarsenobenzene, a yellow, amorphous compound which is readily re-oxidised to the diarsinic acid.

H. W.

## Physiological Chemistry.

**Comparative Studies on Respiration. XXIII. The Effect of Adrenaline on the Production of Carbon Dioxide by Animals and by Plants.** DOROTHY M. HUTCHINSON (*Amer. J. Physiol.*, 1922, 62, 192—196).—Carbon dioxide production was measured by the method of Osterhout (*J. Gen. Physiol.*, 1918, 1, 17). Adrenaline has similar effects on the respiration of frog's muscle and of radish seedlings. Stronger solutions (0.002 to 0.003%) cause a depression, followed by a return to normal, probably as the adrenaline is oxidised. Weaker solutions (0.002 to 0.005%) produce a rhythmic effect; the rate of carbon dioxide production falls, rises, then falls and rises again.

CHEMICAL ABSTRACTS.

**The Mineral Constituents of Blood.** A. DESGREZ and J. MEUNIER (*Compt. rend.*, 1923, 176, 608—611).—A spectrographic analysis of the fractions obtained by crystallisation of the soluble portion of the ash of blood and of serum was made, the photographs being taken on panchromatic plates, and the salts heated in the

hydrogen flame. The first crystal fraction consisted mainly of sodium chloride with traces of potassium. In the next fractions, the potassium line 404 was very pronounced, and the presence of lithium was clearly indicated by the line 670. In the last fractions, the lithium line was as intense as the sodium line 588. The amount of lithium present was estimated at about 1/500 of that of sodium.

G. F. M.

**Blood Studies in the Newborn. Morphological, Chemical, Coagulation, Urobilin, and Bilirubin.** W. P. LUCAS, B. F. DEARING, H. R. HOOBLER, A. COE, M. R. JONES, and F. S. SMYTH (*Amer. J. Diseases Children*, 1921, 22, 525—529).—The blood content of non-protein nitrogen, urea nitrogen, uric acid nitrogen, creatinine nitrogen, sugar, and carbon dioxide has been determined for the first twelve days of life. For this period, the calcium content of the whole blood, corpuscles, and plasma averaged, respectively, 8.8, 5.0, and 12.3 mg., respectively, per 100 c.c. for boys and girls together. During the first four days the coagulation time is definitely increased and the prothrombin element distinctly diminished. Urobilin or urobilinogen could not be found in the faeces. The estimation of bilirubin in plasma was carried out by adding 3 c.c. drop by drop to a solution of 30 c.c. of concentrated hydrochloric acid in 2 litres of 95% ethyl alcohol, and diluting to 25 c.c. On keeping, an emerald-green colour appears, developing greatest intensity in twenty-four hours. Comparison is made in a Hellige colorimeter with a wedge of gelatin, copper sulphate, and India ink, standardised with bilirubin. Eighty-two cases out of ninety gave a positive bilirubin reaction, the average curve beginning with 5 mg. of bilirubin per 100 c.c. of plasma, rising on the third day to 21 mg., and falling on the fourteenth day to 8 mg., although the actual quantities vary with different individuals.

CHEMICAL ABSTRACTS.

**Physiology of the Glands. LIV. Proof of Adrenaline in the Arterial Blood of Animals.** LEON ASHER and CARLO SCHNEIDER (*Biochem. Z.*, 1922, 133, 373—390).—A biological proof is given of the presence of adrenaline in the general circulation.

W. O. K.

**Production of Methæmoglobin by Narcotics.** PH. ELLINGER and FRANZ ROST (*Arch. exp. Path. Pharm.*, 1922, 95, 281—290).—The darkening of arterial blood which occurs during ether or chloroform narcosis is due to the formation of methæmoglobin.

E. S.

**Blood Clotting. V. Alexander Schmidt's Thrombin.** BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1922, 134, 239—249).—With a thrombin solution prepared by Schmidt's method and a fibrinogen solution prepared by Hammarsten's method a number of observations were made which the authors consider prove that the action of thrombin is a pure swelling process, the fibrinogen simultaneously losing its solvent and thereby clotting. Thrombin solution completely freed from protein by various pre-

capitants or by dialysis cannot clot fibrinogen, and the smaller the protein content the longer is the period which elapses before clotting. Clotting time is dependent on the sodium chloride content of the fibrinogen, but is independent of its protein content. When thrombin and fibrinogen solutions of isotonic sodium chloride content were separated by a semipermeable diaphragm, clotting was observed to occur after many hours, even if the thrombin was replaced by gelatin or starch. This is interpreted as being due to the swelling of the partly denatured thrombin at the expense of the fibrinogen which loses its water and clots. H. K.

**Blood Clotting. VI. Mode of Action of Thrombokinase.** BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1922, 134, 250—259).—Thrombokinase was prepared by Morawitz's method from liver. A high temperature and the presence of oxygen produce a feebly active product. The action of thrombokinase is attributed to its effect in lowering surface tension. On keeping, its solutions become more acid and lose activity, the maximum activity being observed over the range  $P_H$  6 to 7. H. K.

**Blood Clotting. VII. The Rôle of Calcium.** BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1922, 134, 260—268).—Oxalated plasma can be caused to clot by addition of strontium salts, but not by barium or magnesium. Calcium is therefore not essential. By means of Traube's viscostagonometer, the internal friction of plasma was determined with increasing oxalic acid content. Increase of the oxalic acid beyond the point of flocculation through neutralisation causes an increased internal friction, and hence an increased ionisation. The same is observed with citrated plasma, and in the region of high internal friction alcohol produces no precipitate. The results are interpreted on the basis that oxalated and citrated plasmas cannot clot owing to maximum ionisation of the fibrinogen-salt complex, and clotting by excess of calcium or strontium salts is due to a reversal of the ionisation of the complex. H. K.

**Adsorption of Protein Degradation Products by the Blood-corpuscles in vivo and in vitro.** B. SEARSKY (*Biochem. Z.*, 1923, 135, 21—31).—Using Bach's method (*A.*, 1917, i, 375) for the estimation of degradation products of protein, the author has investigated the fate of the parenteral administration of erepton and diphtheria toxin to rabbits. No trace of protein degradation product was found in the blood immediately after intravenous injection of erepton (3.5 g.) or toxin (35 c.c.), either in the serum or in the blood, but if the blood is heated to boiling the protein degradation products are recovered quantitatively. The same applies to experiments in vitro. The injected peptones are therefore immediately adsorbed by the corpuscles and the first act in the process of immunisation is the adsorption of the toxins by the corpuscles. H. K.

**The Glycogen Content of White Corpuscles.** L. HABERLANDT (*Biochem. Z.*, 1922, 134, 405—406).—The author suggests

an explanation of de Haan's (A., 1922, i, 484) inability to find an increased glycogen content of the leucocytes of serum exudates after intraperitoneal administration of starch or glucose. H. K.

**The Clinical Significance of the Estimation of Calcium in the Serum of Children, and Possible Errors in the Estimation.** B. KRAMER, F. F. TISDALL, and J. HOWLAND (*Amer. J. Diseases Children*, 1921, 22, 560—564).—The blood-serum of normal children contains 10—11 mg. per 100 c.c., and that of normal adults 9·7—10·8 mg. Changes were observed only in cases of tetany and renal insufficiency, there being more or less distinct diminution of calcium in both cases. Sources of error in the estimation include the presence of calcium in the nitric and trichloroacetic acids, and even distilled water, and in the filter-paper, the solubility of calcium oxalate in water, and the fact that its precipitation must be accomplished in the presence of both magnesium and phosphates. The presence of magnesium in serum and plasma cannot normally be regarded as a serious source of error. Calcium oxalate is best precipitated from a liquid of  $p_H$  5·2—6·2. CHEMICAL ABSTRACTS.

**Antiphenolase (Antilaccase).** A. BACH and W. ENGELHART (*Biochem. Z.*, 1923, 135, 39—45).—Rabbits were immunised by intravenous injections of a phenolase solution prepared from a fungus (*Lactarius vellereus*). The immune sera, produced, inhibited the oxidation of suitable substrates, guaiacol, or pyrogallol independently of the reaction of the medium, whereas normal sera failed to inhibit. The antiphenolase action is associated with the non-dialysable portion of the serum, and is completely destroyed by heating at 80° for thirty minutes. The question as to whether the antiphenolase action is due to a physical change of the immune sera or to production of a chemically defined anti-substances is undecided. H. K.

**The Effect of Codeine on the Digestion of Meat by Dogs.** EDWARD ZUNZ and ALEXIS DELCORDE (*Bull. Soc. chim. Belg.*, 1923, 32, 79—80).—Injections of codeine lengthen the stay, in the stomach, of cooked meat, which is less rapidly affected by the digestive juices. The effects are smaller than those produced by morphine and the other opium alkaloids. Codeine increases the proteoses and decreases the acid albumins in the stomach, similarly affecting the peptones and abiuretic compounds in the prepyloric portion. It does not, however, affect the subsequent contents of the small intestine, and has little effect on the amount of nitrogen present as ammonia-amine type. E. E. T.

**The Influence of Various Quinine Derivatives on the Fermentative Function of the Organism.** J. A. SMORODIN-ZEV and A. N. ADOVA (*Biochem. Z.*, 1923, 135, 128—141).—The authors have investigated the effect of the addition of quinine monohydrochloride, quinine acid sulphate, quinine-urea dihydrochloride, urea nitrate, sulphate, and hydrochloride on the tryptic digestion of casein. The two quinine salts inhibit the action of trypsin, but the quinine-urea complex accelerates the reaction.

The urea salts at dilutions between  $N/20$  and  $N/80$  accelerate the digestion, but urea itself is without action. H. K.

**Ferments of the Digestive Organs of the Bee.** E. SARIN (*Biochem. Z.*, 1923, 135, 59—74).—The distribution of a number of ferments in various sections of the intestinal canal of the bee was examined. Catalase, lipase, amylase, invertase, pepsin, trypsin, and chymosin were found in the stomach, but not in the honey-stomach, the little intestine, or the colon, with the exception of catalase, which was found in the colon in the latter half of winter. Emulsin, lactase, and inulinase were absent in all cases. H. K.

**The Invertase of the Intestinal Canal of the Bee.** E. SARIN (*Biochem. Z.*, 1923, 135, 75—84).—Some further experiments (see preceding abstract) have been carried out on the invertase of the bee. In April and the late autumn, invertase appears to be absent from the bee's stomach, honey at this period consisting mainly of invert-sugar. For the preparation of an active invertase water is best, but the product does not keep well. An extract made with equal parts of glycerol and water retains its activity for eleven months. H. K.

**Unit of Energetic Metabolism and Active Mass of the Organisms.** EMILE F. TERROINE, A. FEUERBACH, and E. BREXCKMANN (*Compt. rend.*, 1923, 176, 462—464).—Analyses of normal and starved subjects in the case of two species show that, although the weight of the animal may vary within wide limits, the nitrogen present expressed as a percentage of the body-weight is a constant. These results, when compared with those of other workers on animals of vastly different size, owing to the difference in species, show that the protein content of the species studied is practically identical. It is thus useless to attempt to establish any relationship directly and entirely between the intensity of metabolism and the protein content. W. G.

**The Influence on Metabolism of some Purine and Pyrimidine Bases.** F. P. UNDERHILL and H. F. FARRELL (*J. Metabolic Research*, 1922, 2, 107—111).—Solutions of caffeine, theobromine, uric acid, and of hypoxanthine when injected into fasting rabbits led to an augmented excretion of total nitrogen, creatine, and creatinine, indicating an increased protein katabolism.

CHEMICAL ABSTRACTS.

**The Influence of Benzyl Benzoate on Nitrogenous Metabolism.** G. T. PACK and F. P. UNDERHILL (*J. Metabolic Research*, 1922, 2, 73—105).—Investigations on dogs indicate that the therapeutic dose of benzyl benzoate for man is probably insufficient to disturb the normal nitrogenous metabolism; larger doses, however (i.e., 0.5 c.c. per kg. of body-weight), cause an increase of protein katabolism in dogs. The total output of nitrogen is increased, marked creatinuria occurs, and conjugated glycuronates appear in the urine, but creatinine metabolism is unmodified. The changes are probably due to benzyl alcohol. Benzyl succinate produces

less change in the normal nitrogenous metabolism of the dog than the other benzene derivatives investigated. The katabolic processes which ensue after the administration of these benzene derivatives are discussed theoretically.

CHEMICAL ABSTRACTS.

**Potassium in Animal Nutrition. I. Influence of Potassium on Urinary Sodium and Chlorine Excretion.** HARRY G. MILLER (*J. Biol. Chem.*, 1923, 55, 45—59).—Experiments on pigs have shown that the increased excretion of sodium and chlorine which follows the administration of a single large dose of potassium salts is not maintained, even when the inclusion of potassium salts in the diet is continued.

E. S.

**Potassium in Animal Nutrition. II. Potassium in its Relation to the Growth of Young Rats.** HARRY G. MILLER (*J. Biol. Chem.*, 1923, 55, 61—78).—Rats maintained on diets containing less than approximately 0.1% of potassium showed failure of growth. Subsequent increases in the potassium content of the diet produced no permanent improvement.

E. S.

**Hydrolysis of Higher Fats in Egg-secretion.** OTTO GLASER (*Biol. Bull. Marine Biol. Lab.*, 1922, 46, 68—74).—*Arbacia* egg-secretion has the power to hydrolyse higher fats. Since whale oil, olive oil, and cetyl butyrate do not occur in sea urchin eggs, the lipase present must be non-specific. The lipolysin isolated by Woodward (cf. *J. Exp. Zool.*, 1918, 26, 459) appears to be, or contain, that enzyme which in unmodified egg-water is responsible for the hydrolysis of the higher fats.

CHEMICAL ABSTRACTS.

**Chemistry of the Lung. Nucleic Acids of the Lung.** UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 133, 405—408).—A nucleic acid has been separated from lung tissue and purified by repeated precipitation as the copper salt. It has the formula  $C_{33}H_{54}O_{24}N_{10}P_2$ , and when hydrolysed with methyl-alcoholic hydrochloric acid yields adenine and guanine. No pentose could be detected.

W. O. K.

**Production and Destruction of the Cholesterol of the Spleen during Aseptic Autolysis.** SALVATORE MARINO (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 192—195).—The author confirms the observation of Abelous and Soula (*Compt. rend. Soc. Biol.*, 1920) that, during aseptic autolysis of the spleen, the cholesterol content at first increases and subsequently diminishes. The liver and brain show similar behaviour, but with the suprarenal and thyroid glands and the kidneys only destruction of the cholesterol occurs. These phenomena are functions of the temperature and time. It thus appears that, more than other organs, the spleen exerts a marked influence on the formation of cholesterol and on the metabolism of fats.

T. H. P.

**Creatine Content of Muscle in Anaërobic Contraction.** E. A. SPIEGEL and A. Löw (*Biochem. Z.*, 1923, 135, 122—127).—The creatine content of the gastrocnemius muscles of frogs is not altered by stimulating them to exhaustion either in Ringer solution or in air or nitrogen.

H. K.

**Acetaldehyde as an Intermediate Metabolic Product in Surviving Muscle.** JULIUS HIRSCH (*Biochem. Z.*, 1922, 134, 415—423).—In the aqueous distillate from the muscles of frogs, acetaldehyde was detected by Rimini's colour reaction. By the use of a fixative, dimethylhydroresorcinol, acetaldehyde was isolated from the surviving muscles of carp and tench. The breakdown of carbohydrates or lactic acid in the animal body appears to be by way of acetaldehyde. H. K.

**Manganese in Hair.** J. McCRAE (*J. S. African Chem. Inst.*, 1923, 6, 18—19).—The ash from 2.5 to 10 g. of hair was evaporated to dryness with dilute nitric acid, and the residue extracted with boiling water acidified with the same acid. To the filtered extract a few drops of dilute silver nitrate were added and then a small quantity of concentrated ammonium persulphate. Depending on the quantity of manganese present, a more or less deep pink colour is developed. It was matched by dilution of  $N/2000$  solution of potassium permanganate. Five samples of hair varying from fair to very dark were thus examined, and the quantity of manganese found to be of the order of 1 to 2 parts per million of hair. No relation with the colour was observed. The small proportion probably arises from the manganese in vegetable matter, which in turn is derived from that widely distributed in rocks and soil. T. S. W.

**The Reduction of Nitro-groups by Living Tissues.** N. WATERMAN and J. KALEFF (*Biochem. Z.*, 1923, 135, 174—181).—Lipschitz's results (*A.*, 1921, i, 203), on the reduction of *m*-dinitrobenzene by excised tissues and tumours, from which he draws important conclusions controverting the more direct results obtained by others with the Barcroft differential apparatus, are shown to be due to the use of impure *m*-dinitrobenzene, possibly containing thiophen derivatives. H. K.

**Calcium Content of Cats treated with Calcium.** W. HEEBNER and P. RONA (*Biochem. Z.*, 1923, 135, 248—281).—The minimum content of calcium oxide of the muscles, liver, brain, and kidneys of normal cats lies between 5 and 7 mg. of the weight when fresh; of the heart and small intestine 11 mg., lungs 16 mg., and colon between 25 and 30 mg. After repeated subcutaneous administration of calcium chloride solution (2 to 5%) the only organ showing increased calcium content is the kidney. H. K.

**The Inorganic Constituents of Marine Invertebrates.** FRANK WIGGLESWORTH CLARKE and WALTER CALHOUN WHEELER (*U.S. Geol. Survey*, 1922, Professional Paper 124, 1—62).—Quantitative analyses have been made of the inorganic constituents of a large number of marine invertebrates, and of marine algae. The results of previous analyses by other workers are also quoted in the paper, and the general results are discussed in their bearing more particularly on geological problems. W. O. K.

**Occurrence of Copper and Zinc in certain Marine Animals.** HAZEL W. SEVERY (*J. Biol. Chem.*, 1923, 55, 79—91).—Estimations have been made of the copper and zinc content of sixteen

different marine animals. Zinc was present in every case. Copper, however, was absent, or practically so, from the mammals (whale, sea-lion), and also from the clam. E. S.

**Is the Taste of a Salt due to the Ions or to the Whole Molecule?** H. KIONKA and F. STRÄTZ (*Arch. exp. Path. Pharm.*, 1922, **95**, 241—257).—Results obtained with the chlorides, bromides, and iodides of the alkali metals and ammonia indicate that the kation is mainly responsible for the intensity  
( $\text{NH}_4 > \text{Na} > \text{Li} > \text{Rb} > \text{Cs} > \text{K}$ )

and the anion for the quality of the taste. Neither quality nor intensity is appreciably altered by the presence of tasteless colloids (starch). Sodium chloride has a pure saline taste; all the remaining salts examined have mixed tastes, amongst which no fewer than twenty-five distinct tastes have been distinguished. E. S.

**Oxidation of Reduced Glutathione and other Sulphydryl Compounds.** MALCOLM DIXON and HUBERT ERLIN TUNN. CLIFFE (*Proc. Roy. Soc.*, 1923, [B], **94**, 266—297).—Experiments are described which show that the reduction of methylene-blue by reduced glutathione (this vol., i, 167), cystein, or thioglycollic acid are autocatalytic reactions in which the disulphide form of the sulphur compound acts as catalyst. This action is probably due to the formation of an additive compound between the sulphydryl and disulphide forms which is more active than the former alone. Acceleration of the reaction is also produced by surfaces such as glass-wool, kieselguhr, and platinum-black, provided care is taken to remove all traces of oxygen, and by direct sunlight. The oxidation of the sulphydryl compounds by atmospheric oxygen is similarly autocatalytic. In the cases of glutathione and cystein, the reaction velocity shows an optimum at  $P_H$  7.4; this, however, is not characteristic of sulphydryl groups, since it is not shown by thioglycollic acid. E. S.

**The Inorganic Phosphate content of Breast Milk of Mothers with Normal and with Rachitic Infants.** L. VON MEYSENBUG (*Amer. J. Diseases Children*, 1922, **24**, 200—203).—Average samples of the milk of mothers of non-rachitic and rachitic infants contain, respectively, 2.5—6.2 (average 4) mg. and 2.7—5.7 (average 4.8) mg. of inorganic phosphate per 100 c.c. The serum of non-rachitic and rachitic infants contained, respectively, 4.1—5.8 (average 5) mg. and 2.2—4.1 (average 2.8) mg. of inorganic phosphate per 100 c.c. CHEMICAL ABSTRACTS.

**Arginase. VII. Arginase in the Enteric Mucus and in the Enteric Secretion.** ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 559—561).—By the method previously described (this vol., ii, 271) the author demonstrates the absence of arginase from the intestinal secretion of the dog, the conclusion being drawn that arginase is not, as is sometimes assumed, an extracellular digestive enzyme participating in the digestion of proteins in the intestinal tract. On the other hand, this enzyme occurs in the intestinal mucus of the dog or monkey, probably

because it plays a part in the synthesis of homogeneous proteins from the products of digestion of heterogeneous proteins, this process being necessarily accompanied by partial destruction or elimination of certain amino-acids.

T. H. P.

#### **Behaviour of Cholesterol in the Blood and in the Kidneys.**

LOTHAR TIETZ (*Frankfurter Z. Pathol.*, 27, 353—367; *Ber. ges. Physiol.*, 15, 93; from *Chem. Zentr.*, 1923, i, 176).—The elimination of cholesterol in the urine appears to be independent of the amount present in the blood. Occurrence of cholesterol in urine implies deposition of fat in the renal parenchyma.

G. W. R.

**Elimination and Destruction of Uric Acid in the Human Body.** HEINRICH CHANTRAINE (*Biochem. Z.*, 1922, 133, 613—625).—It appears that fluctuations in the mechanism of elimination rather than of production are responsible for the variations in the daily excretion of uric acid. If uric acid is administered as the sodium salt, no destruction seems to take place, and approximately the amount administered is eliminated in the urine during the next three or four days, in addition to the normal elimination.

W. O. K.

**Analysis of the Urine Colouring Matters. III. Urochrome.** M. WEISS (*Biochem. Z.*, 1922, 133, 331—349).—Urochrome does not exist primarily in the urine as such, but as urochromogen, derived apparently from the destruction of cells. Urochromogen is the cause of the Ehrlich diazo-reaction. When oxidised, which is easily effected by atmospheric oxygen in alkaline solution, it is converted into the coloured compound urochrome, or into uromelanin.

W. O. K.

**Analysis of Urine Colouring Matters. IV. The Diazo-reaction of Urine and Urochromogen Excretion.** M. WEISS (*Biochem. Z.*, 1922, 134, 269—291).—The red colour produced in urine by Ehrlich's reagent is due almost entirely to urochromogen.

H. K.

**The Metabolism of Inorganic Materials in Diabetics. I.** ROBERT MEYER-BISCH and PAUL THYSSSEN (*Biochem. Z.*, 1923, 135, 308—316).—In four cases of diabetes mellitus the authors have estimated the calcium, dextrose, sodium chloride, sulphuric acid (free and bound) content and the alkali reserve of the blood after administration of 50 g. of sodium hydrogen carbonate. In each case the alkali reserve fell off, the other quantities showing little alteration, except calcium, which remains constant in normal persons but sometimes exhibits a temporary depression in a diabetic.

H. K.

**The Glycogen Content of the Tissues of Diabetic Animals and the Influence of Adrenaline thereon.** A. I. RINGER, H. DUBIN, and F. H. FRANKEL (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 92—97).—Between the second and seventh day of glycosuria, the muscles of fasting dogs given daily injections of phloridzin were found to contain on an average 482, 306, 228, 155, and 138 mg.

of glycogen per 100 g. Despite continuous fasting and complete diabetes, the muscle-cells retained a certain amount of residual glycogen. The muscles of similarly phloridzinised dogs, which had also been injected with adrenaline on the second or third day of glycosuria, contained the following amounts of glycogen in mg. per 100 g. one, three, and five days, respectively, after the adrenaline injection: 0; 20, 33, 23, 39; 69. In the case of dogs rendered glycogen-free and given glycogenetic substances, such as glycine, alanine, propionic acid, and lactic acid, the resulting glycosuria was not comparable to that found in dogs not treated with adrenaline. It is concluded that fasting diabetic dogs possess the power of glycogen formation after that substance has been eliminated from the muscles by the administration of adrenaline, and that failure of glycosuria is not a criterion of the glycogenetic quality of a substance, when given to deglycogenised diabetic animals.

CHEMICAL ABSTRACTS.

**Is there More Than One Kind of Rickets?** P. G. SHIPLEY, E. A. PARK, E. V. MCCOLLUM, and NINA SIMMONDS (*Amer. J. Diseases Children*, 1922, 23, 91—106).—There are two main kinds of rickets. In the one, the calcium content of the blood is normal, or nearly so, and the inorganic phosphorus content low, whilst in the other the relation is reversed.

CHEMICAL ABSTRACTS.

**Calcium and Phosphorus in the Serum in Relation to Rickets.** J. HOWLAND and B. KRAMER (*Amer. J. Diseases Children*, 1921, 22, 105—119).—For the estimation of inorganic phosphates, the blood-serum should not be left in contact with the blood clot. The inorganic phosphorus content of the serum of sixteen non-rachitic children varied from 4 to 7.1 mg. per 100 c.c. (average 5.4 mg.). For partly or wholly breast-fed infants, the range was 5.6—7.1 mg. (average, 6.1 mg.). The calcium content of the serum of fourteen cases of rachitic infants without signs of latent tetany varied from 8 to 10.8 mg. per 100 c.c.; the phosphorus content 0.6 to 3.2 mg., in four cases the magnesium content being 1.8—2.5 mg. In some cases, the administration of cod-liver oil caused a decided increase in the amount of inorganic phosphorus.

CHEMICAL ABSTRACTS.

**Calcium and Phosphorus Metabolism. I. The Excretion of Calcium and Phosphorus. II. The Metabolism of Calcium and Phosphorus in Rickets.** S. V. TELFER (*Quart. J. Med.*, 1922, 16, 45—62; 62—72).—I. The excretion of calcium, phosphorus, and their fatty derivatives is interdependent, calcium being eliminated chiefly as the phosphate and to a less extent as insoluble soaps. The total amount of calcium and phosphorus eliminated is nearly proportional to the intake; a large part of the ingested calcium is not absorbed, and appears in the faeces as normal calcium phosphate, only a small fraction of the total calcium being excreted in the urine. There is no evidence that any appreciable amount of endogenous calcium or phosphorus is eliminated. In normal infants, 40% of the total phosphorus excreted appears in

the urine and 60% in the fæces, but with acid formation in the intestine a greater proportion is excreted in the urine. The degree of deviation of phosphorus to the urine is roughly proportional to the amount of fatty acids in the fæces, and, therefore, to the degree to which fatty acids had displaced phosphoric acid from its normal combination with calcium in the intestine. An excess of calcium restricts an increased amount of phosphorus in the intestine. When the fat and phosphorus intake was low, an excess of calcium rendered the urine free from phosphorus. The average daily faecal weight depends chiefly on the degree to which calcium soaps are formed, since these form a mechanical basis for the formation of fæces. When the intake of both fat and phosphorus is very deficient, calcium may be excreted as carbonate. No evidence was found of the absorption of calcium and phosphorus in excess of requirements, with re-excretion into the intestine.

II. In normal infants on a diet of cow's milk the retentions of lime and phosphate were approximately equal. An excess of phosphate is retained over the equivalent amount of lime required for bone formation. In rickets, there is diminished retention of lime and phosphate, the latter being possibly due to diminished fixation by the calcium. No negative retentions of lime or phosphate were found, so that it does not appear that bone softening in rickets is due to excessive decalcification.

#### CHEMICAL ABSTRACTS.

##### The Mechanism of the [Physiological] Action of Chlorates.

RUDOLF L. MAYER (*Arch. expt. Path. Pharm.*, 1922, 95, 351—377).—In the presence of either ferrous sulphate or hæmoglobin, potassium iodide is oxidised by potassium chlorate. In both cases, the reaction is similarly influenced by variations in acidity, temperature, and concentration. The author concludes that the reduction of chlorates in the blood is a catalytic reaction in which hæmoglobin acts as catalyst by virtue of the iron which it contains. Hæmoglobin also catalyses the oxidation of sodium sulphite by potassium chlorate; when the sulphite is completely oxidised, the production of methæmoglobin commences. The latter can be partly reduced if more sulphite is added immediately, but if time is allowed to elapse, the reduction is more incomplete. Apparently the methæmoglobin changes from an active to an inert form. E. S.

Pharmacology of Selenium and Tellurium. IV. Action of their Acids on Trypanosomes in vitro. FRITZ LEHMANN (*Biochem. Z.*, 1922, 134, 390—397).—High concentrations of selenium or tellurium are lethal to trypanosomes, but after one hour's exposure the following dilutions were not lethal: for tellurites 1:500, for tellurates 1:300, for selenites 1:500, and for selenates 1:100. It was not found possible to obtain exact figures of toxicity. H. K.

Toxicity and Actions of the Normal Butylamines. P. J. HANZLIK (*J. Pharm. Expt. Ther.*, 1923, 20, 435—449).—The pharmacological actions of mono-, di-, and tri-butylamines have been

studied. All are toxic, and act as cardiac depressants; on the smooth muscle of excised organs, however, they exert a stimulant action, thus resembling histamine. When placed in an atmosphere saturated with the vapours of mono- and di-butylamines, white rats rapidly succumb; tributylamine, on the other hand, is insufficiently volatile to produce this effect.

E. S.

**The Effect of the Parenteral Administration of some Amino-acids on the Respiratory Gas Exchange of the Dog.** F. W. KRZYWANEK (*Biochem. Z.*, 1923, 134, 500—527).—The parenteral administration of alanine and of glycine causes a rise in the respiratory quotient and a negative nitrogen balance. The results of the author and of other investigators are discussed at length.

W. O. K.

**Pharmacological Properties of some isoUrea Derivatives.** STEWARD BASTERFIELD (*J. Pharm. Expt. Ther.*, 1923, 20, 451—461).—The *O*-ethyl derivative of allophanic ester,  $\text{NH}_2\text{C}(\text{OEt})\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p.  $39^\circ$ , when injected into rabbits produced a moderate depression, a rapid fall of body temperature, and an increased muscle tonus. No great physiological action was shown by other iso-urea derivatives.

E. S.

**The Chemical Defence Mechanism of the Fowl.** JAMES H. CROWDLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1923, 55, 15—31).—Various substances were fed to fowls. Benzaldehyde, phenylpropionic acid, and cinnamic acid were excreted as ornithuric acid; *p*-hydroxybenzaldehyde as *p*-hydroxybenzoic acid; *m*-nitrobenzaldehyde probably as the anhydride of *m*-aminobenzoic acid; nitrobenzene as *m*-aminophenol; *o*-nitrophenylpropionic acid as *o*-nitrobenzoic acid, and *m*-aminobenzoic acid as *m*-acetamidobenzoic acid. The fowl employs, apparently, processes of oxidation, reduction, acetylation, and conjugation with ornithine for the detoxication of these compounds, but is unable to form carbamide-compounds or to furnish glycine for this purpose.

E. S.

**The Active Alkaloids of Ergot.** H. H. DALE and K. SPIRO (*Arch. expt. Path. Pharm.*, 1922, 95, 337—350).—The physiological actions of the two alkaloids ergotoxine,  $\text{C}_{35}\text{H}_{41}\text{O}_6\text{N}_5$  (Barger and Carr, T., 1906, 94, 89), and ergotamine,  $\text{C}_{33}\text{H}_{35}\text{O}_5\text{N}_5$  (Spiro and Stoll, A., 1922, i, 47), isolated from ergot are qualitatively and quantitatively identical.

E. S.

**The Influence of the Parenteral Introduction of Protein on the Gas Metabolism.** ALFRED LEIMDÖRFER (*Biochem. Z.*, 1922, 133, 409—416).—Protein introduced parenterally into animals causes an increased oxidation in the tissues with a corresponding rise in temperature.

W. O. K.

**Effect of Pancreatic Extract (Insulin) on Normal Rabbits.** F. G. BANTING, C. H. BEST, J. B. COLLIP, J. J. R. MACLEOD, and E. C. NOBLE (*Amer. J. Physiol.*, 1922, 62, 162—176; cf. *Trans. Roy. Soc. Canada*, 1922, 16, V, 1).—When injected subcutaneously

into normal rabbits, insulin causes a diminution of the sugar content of the blood within a few hours, the animal exhibiting signs of hunger and thirst, hyperexcitability, and apparent fear, convulsive seizures often supervening, the sugar content of the blood then usually being about 0.045%. Subcutaneous injections of dextrose act as an antidote to the convulsions and other symptoms. Post-mortem examination frequently discloses a peculiar mucigenous degeneration of the subcutaneous tissues of the abdominal wall. As a basis for the physiological assay of insulin, the authors suggest as one unit the number of c.c. which cause the blood-sugar of normal rabbits to fall to 0.045% within four hours. This dose is decidedly active in lowering the sugar content of the blood in diabetic patients. CHEMICAL ABSTRACTS.

[Physiological] Effect of "Arsylene." S. KATZENELBOGEN (*Arch. internat. pharm. therap.*, 1922, 26, 407—420; from *Chem. Zentr.*, 1923, i, 173).—Arsylene (sodium allylarsinate) is less poisonous than arsenious oxide. With single administration of a large dose, no simple alteration in the composition of the blood is observed. Daily doses of 0.015 g. per kg. of live weight produce slight decrease in erythrocytes, irregular variation in leucocytes, increase in lymphocytes, and occurrence of isolated nucleated erythrocytes. Daily doses of 0.001—0.002 g. per kg. produce irregular increase in erythrocytes and hæmoglobin. The resistance of erythrocytes against hæmolysis is not increased by "arsylene." G. W. R.

**Experimental Acid Poisoning. II. The Respiratory Gas exchange in Acid Poisoning.** A. LOEWY and E. MÜNZER (*Biochem. Z.*, 1923, 134, 437—441).—The administration of hydrochloric acid to rabbits decreases the intake of oxygen as well as the output of carbon dioxide. The deleterious poisoning effects of the acid are therefore to be ascribed to a decrease in the rate of oxidation in the cell, as well as to the lowered capacity of the blood to transport carbon dioxide. W. O. K.

**Experimental Acid Poisoning. III. Does Methyl Alcohol poisoning Lead to an Acidosis?** A. LOEWY and E. MÜNZER (*Biochem. Z.*, 1923, 134, 442—446).—In acidosis, there is a change in the dissociation constant of the blood. Methyl alcohol is said to be oxidised to formic acid in the body, and the abnormal amount of ammonium salts in the urine following methyl alcohol poisoning is said to be a result of the acidosis. It is now shown that if methyl alcohol is administered to dogs or rabbits, any acidosis so induced is too weak to alter the dissociation curve of the blood. W. O. K.

**A Study of Metabolism in Chloroform Poisoning.** F. P. ANDERHILL and ROBERT KAPSINOW (*J. Metabolic Research*, 1922, 5, 57—72).—Graham's hypothesis (*J. Exp. Med.*, 1915, 22, 48) that in late poisoning with chloroform and with other alkyl halides the intoxication is due chiefly to the liberated hydrogen chloride was not confirmed. A diet yielding an alkaline ash when fed to

rabbits had no inhibiting effect on delayed chloroform poisoning. The excretion of chlorine by rabbits poisoned with chloroform was not increased in starvation. The only metabolic changes observed with the alkaline diet that could not be explained by the food were alterations in the creatinine, creatine, and total nitrogen excretion. These are probably the results of absorption of dead tissue following injury by chloroform. CHEMICAL ABSTRACTS.

## Chemistry of Vegetable Physiology and Agriculture.

**Influence of Copper on Lactic Fermentation.** MARC FOUASSIER (*Compt. rend.*, 1923, 176, 606—608).—The influence exercised on lactic fermentation by contact with certain metals either previously to, or during the action of, the ferment was studied. Lamellæ of the following metals, zinc, aluminium, lead, silver, iron, nickel, copper, and tin, were placed in contact with sterilised milk, which was then inoculated with the lactic ferment, and observations were made of the increase in acidity. It was found that this increase was more rapid in presence of iron, much retarded by copper, and uninfluenced by the other metals. The inhibiting action of the metallic copper on the fermentation was just the same, whether the metal was present during the fermentation or whether the milk had previously been exposed for eight hours to the metal, which was then removed before inoculation. The antiseptic action of copper was further demonstrated by the gradual loss in activity of the ferment suspended in pure sterile water in presence of a piece of copper foil. G. F. M.

**Bacteria which Split Nucleoprotein and their Importance for the Liberation of the Phosphorus Reserve in Surface Soils.** ALFRED KOCH and ALICE OELSNER (*Biochem. Z.*, 1922, 134, 76—96).—Phosphates are liberated from nucleoproteins and their breakdown products by various soil bacteria (nucleobacter). Chalk is suitable to the liberation of inorganic phosphate, as it gives an alkaline reaction favourable to the bacteria. For analyses of inorganic phosphate in presence of organically bound phosphorus, ammonium molybdate was found suitable, and ultra-filtration was employed for removing bacteria from nutrient media before analysis. H. K.

**The Chemotherapy of the Acridine Dyes in Experimental Tuberculosis.** MAURICE I. SMITH (*J. Pharm. Expt. Ther.*, 1923, 20, 419—434).—Certain acridine derivatives, namely, acriflavine, proflavine, acridinium-yellow, and acridine-orange, inhibit to a marked degree the growth of the tubercle bacillus in vitro. The pathogenicity of the bacillus is not, however, altered, neither is the tuberculosis process in experimentally infected animals modified by injections of these substances. E. S.

**Occurrence of *p*-Hydroxybenzaldehyde and *p*-Hydroxybenzoic Acid in the Bacterial Decomposition of Tyrosine, with Special Reference to Melanin Formation.** KINSABURO HIRAI (*Biochem. Z.*, 1923, 135, 299—307).—By the prolonged action of *Proteus vulgaris* on *l*-tyrosine in Ringer's solution, *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid were formed in small yield. In addition, after three weeks a black colouring matter was produced, but not if the medium contained glycerol. The production of this melanin is favoured by use of Henderson's phosphate mixture as a nutrient medium, or by the presence of platinum sponge. The melanin is amorphous, but is soluble in alkali, alcohol, glacial acetic acid, acetone, or ethyl acetate. Its production is probably due to a tyrosinase, as under parallel conditions it is not formed from tryptophan, phenylalanine, or leucine.

H. K.

**Oxidation of Zinc Sulphide by Micro-organisms.** W. RUDOLFS and ANDRÉ HELBRONNER (*Soil Sci.*, 1922, 14, 459).—A culture of organisms was isolated which were capable of oxidising zinc sulphide to sulphate without suffering injury from the soluble zinc salt. The addition of elementary sulphur to an impure culture increased the rate of oxidation of zinc sulphide. The "Lipman" sulphur oxidising bacteria produce sufficient sulphuric acid to dissolve zinc carbonate and silicate. The possibility of a biological process for utilising low-grade zinc blendes is noted.

A. G. P.

**Cell Respiration. I. The Respiration of Yeast-cells.** P. RONA and K. GRASSHEIM (*Biochem. Z.*, 1922, 134, 146—162).—The optimum hydrogen-ion concentration, whether produced by phosphate or acetate buffer mixtures, for the respiration of yeast-cells (*Torula pulcherrima*) lies between  $P_H$  4.5 and 6.6. Just outside these limits, the respiration falls off considerably. The oxygen consumption, using acetates as buffers, is about 30% more than when using phosphates, the most favourable concentration of the latter being one-third molar. The respiration is affected by the age of the yeast, for it falls off after seven days; it is not, however, affected by repeated freezing and thawing of the yeast-cells.

H. K.

**The Transformation of Tertiary Amino-acids by Yeast.** K. KURONO (*Biochem. Z.*, 1922, 134, 424—433).—When a large amount of sucrose was fermented by yeast in the presence of *dl*-2-amino-2-methyl-*n*-valeric acid, the products isolated were the same amino-acid exhibiting *lævo*-rotation, and methylpropylcarbinol also exhibiting *lævo*-rotation. The identity of this alcohol was proved by preparation of its  $\alpha$ -naphthylurethane, m. p. 46°, by its oxidation to methyl propyl ketone, which gives a *p*-nitrophenylhydrazone, m. p. 112°. During the fermentation, it is therefore supposed that the degradation takes place via the ketone,  $\text{NH}_2\text{CRR}'\text{CO}_2\text{H} \rightarrow \text{CORR}' \rightarrow \text{CHRR}'\text{OH}$ .

H. K.

**The Behaviour of Pyruvic Acid and Acetaldehyde to Oxygenated Yeast.** FRITZ LIEBEN (*Biochem. Z.*, 1923, 135, 240—247).—Pyruvic acid as its sodium salt is partly decomposed with evolution of carbon dioxide and partly utilised by the yeast-cells for body building, when shaken with yeast-cells in a stream of oxygen. Acetaldehyde under similar conditions is for the most part unchanged. Pyruvic acid can be quantitatively estimated by Fürth and Charnass's method if it be first of all reduced to lactic acid by zinc dust and hydrochloric acid. H. K.

**The Oligodynamic Action of Metals.** JOSEF SCHUMACHER (*Biochem. Z.*, 1922, 134, 398—404).—Pure methylene-blue reduced to leucomethylene-blue by sodium formaldehydesulphoxylate can be used for detecting silver in oligodynamic quantities. Water in which a silver coin has been boiled restores the blue colour instantaneously, and immersion of the coin in a leucomethylene-blue solution gives rise to blue layers over the coin, whereas the main bulk of the solution remains colourless. H. K.

**The Influence of Hydrogen-ion Concentration on the Antiseptic Effect of Sublimate.** GEORG JOACHIMOGLU (*Biochem. Z.*, 1923, 134, 489—492).—The antiseptic effect of mercuric chloride disappears in weakly alkaline reaction between  $P_H$  7.8 and  $P_H$  10.1, and appears to be most marked in weakly acid reaction between  $P_H$  5.0 and  $P_H$  6.6. W. O. K.

**Formation of Oxygen from Carbon Dioxide by Protein-Chlorophyll Solutions.** M. EISLER and L. PORTHEIM (*Biochem. Z.*, 1923, 135, 293—298).—The filtrate from a 95% alcoholic extract of grass was treated with four volumes of twenty-fold diluted heteroserum and the flocculated precipitate collected by centrifuging. The protein-chlorophyll mixture was dissolved in 0.85% sodium chloride solution, and using a differential blood-gas apparatus the solution in one bulb was exposed to bright sunlight in an atmosphere of carbon dioxide. The bulb exposed to sunlight exhibited an excess pressure which analysis showed was due to liberation of oxygen. H. K.

**A New and Efficient Respirometer for Seeds and other Small Objects.** GEORGE T. HARRINGTON and WILLIAM CROCKER (*J. Agric. Res.*, 1923, 23, 101—116).—After discussing various types of respirometers, previously advocated, the authors describe a new form of respirometer, a sketch of which is given in the original. With this apparatus, oxygen consumption and carbon dioxide production are determined in the same apparatus and for the same period of time, using the whole volume of air instead of a sample. The gaseous exchanges are determined at the end of an experimental period by means of a manometer, which is an integral part of the apparatus. The pressure readings are made the basis of direct calculations, both of oxygen consumed and of carbon dioxide given off. W. G.

**Respiration of Apple Seeds.** GEORGE T. HARRINGTON (*J. Agric. Res.*, 1923, 23, 117—130).—Using the respirometer previously

described (preceding abstract), the author has made a study of the respiration of apple seeds under different conditions.

The respiratory intensity of dormant apple seeds is low, but the intensity in the case of seeds capable of germination is higher and becomes very high with advancing germination, but soon falls if the germinated seeds are kept at too high a temperature. Removal of the outer seed coats increases the respiratory intensity and accelerates germination, but does not affect the respiratory quotient. At the ordinary temperature, the respiratory quotient corresponds with complete oxidation of fats or only slight increase in sugars. With rise in temperature, there is an increase in the respiratory quotient, causing impoverishment in easily oxidisable substances, and with fall in temperature there is a fall in the quotient and a storage of oxygen which probably leads to an increase in acids and sugars. With a relatively high rate of oxidation at high temperatures, there is a tendency for the seeds to become dormant. With advancing germination, the respiratory quotient becomes low, indicating the rapid transformation of fats and accumulation of sugars, but this is preceded by a brief initial rise, which indicates that oxygen-rich substances are being broken up more rapidly than they are replaced.

Respiratory intensity, respiratory quotients, and temperature coefficients are affected by the previous treatment of the seeds, being higher after treatment which tends towards after-ripening, and lower after treatment which induces deeper dormancy. W. G.

**Ferment Formation in Germinating Plant Seeds.** A. BACH and A. OPARIN (*Biochem. Z.*, 1922, 134, 183—189).—The authors have estimated the content of respiratory ferments (catalase, peroxidase, oxygenase) and of hydrolytic ferments (amylase, protease) in germinating wheat grains and sunflower seeds. During germination, the content of ferments rises to a maximum in six to eight days except for catalase in wheat, which reaches its maximum in three to four days. The catalase content of sunflower seeds is greater than that of wheat, but the reverse is the case for the other ferments. H. K.

**The Influence of Oxygen on the Formation of Ferments in Germinating Wheat Grains.** A. OPARIN (*Biochem. Z.*, 1922, 134, 190—193).—Increased partial pressure of oxygen has no influence on the formation of ferments (preceding abstract) with the exception of oxygenase, which is inhibited, but replacement by an inert gas such as hydrogen is inimical to all ferments except oxygenase. H. K.

**Ammonia as Primary and End-product of Nitrogen Metabolism in Plants.** D. N. PRIANISCHNIKOV (*Landw. Versuchs-Stat.*, 1922, 99, 267—286).—The author further develops his earlier theories on the nitrogen metabolism of plants. In seedling plants receiving ammonium salts, the changes depend on the amount of carbohydrates present. Where, as in barley and maize, abundant carbohydrate is present, asparagine is formed and comparatively little ammoniacal nitrogen is found. Where, as in

lupines, the proportion of carbohydrate to protein is less, more ammoniacal nitrogen is found, and the formation of asparagine is depressed. By artificially decreasing the amount of carbohydrate, either by starvation or by removal of cotyledons or endosperm, plants rich in carbohydrate can be made to behave in the same way as those poor in carbohydrate. Similarly, by supplying dextrose to lupine seedlings, increased formation of asparagine and decrease in ammoniacal nitrogen may be induced. Asparagine is held to fulfil the same function in plant metabolism as carbamide in animal metabolism.

G. W. R.

**The Chemical Mechanism of the Formation of Fat in the Living Cell.** HUGO HAEHN and WALTER KINTROP (*Ber.*, 1923, 56, [B], 439—445).—A preliminary communication. It has been suggested previously (Haehn, *Z. tech. Biol.*, 1921, 9, 217) that acetaldehyde is an intermediate product in the conversion of carbohydrates into fats within the living cell, and that the process occurs in accordance with the scheme: dextrose  $\rightarrow$  pyruvic acid  $\rightarrow$  acetaldehyde  $\rightarrow$  aldol  $\rightarrow$  glyceryl ester. It is suggested that aldol is transformed into  $\gamma$ -dihydroxy-*n*-hexaldehyde or the corresponding unsaturated substance, which is converted by successive oxidation and reduction into sorbic and hexoic acids. Condensation of three molecules of the unsaturated aldehyde leads to the production of the carbon chain of oleic and stearic acids, whereas that of palmitic acid is derived from two molecules of hexaldehyde and one molecule of aldol. In the present communication, it is shown that the assumed intermediate products are assimilated by the cell, and that the presence of certain of them can be established by suitable methods.

*Endomyces vernalis* is grown in a normal culture solution which is replaced as soon as the mycelium is developed by pure solutions of acetaldehyde, pyruvic acid, or aldol, respectively, which are adjusted to  $P_H$  6.8 by potassium hydrogen phosphate. In every case, the appearance of fat within the cells is noticed within twenty-four hours. Similar observations are recorded with maltose. The process of fat formation probably occurs in two phases, in the first of which the sugar is converted by zymase through pyruvic acid into acetaldehyde, probably in accordance with Neuberg's scheme of alcoholic fermentation; the hypothesis receives support from the observation that carbon dioxide is freely evolved, whereas the presence of ethyl alcohol cannot be detected. In the second phase, the synthesising enzymes, probably of the carboligase type, cause the formation of fat from the acetaldehyde.

The formation of acetaldehyde as intermediate product has been demonstrated by the aid of the sulphite process; in experiments in which the acetaldehyde is thus fixed, the production of fat is very small. The yields of acetaldehyde correspond approximately with those obtained by Neuberg in experiments with moulds.

For the estimation of fat, the mould is dried at  $100^\circ$  and cautiously heated in an iron crucible with water and solid potassium hydroxide. The molten mass is cooled, dissolved in water, and acidified

with sulphuric acid. The free fatty acids are extracted with light petroleum, dissolved in alcohol, and titrated with alcoholic potassium hydroxide solution; the results are expressed as triolein. H. W.

**The Genesis of Peroxydase in Plants. Conditions determining Fission of Peroxydase from the Protoplasts and Liberation in the Cell-juice.** W. PALLADIN and (FRL.) S. MANSKAJA (*Biochem. Z.*, 1923, 135, 142—157).—Using the colour reaction given by peroxydase with guaiacum-resin or guaiacol and hydrogen peroxide, peroxydase is found in the cell-sap, but also found in the protoplasts. During autolysis, the peroxydase is split off from the protoplasts, and especially so in the presence of salts. The results are interpreted in terms of Ehrlich's side-chain theory, the postulated existence of pro-ferments being unnecessary. Peroxydase is also found in the woody fibre of the beech. H. K.

**The Constituents of Green Plants. XXIII. Malic Acid in Plants.** HARTWIG FRANZEN and ERNST KEYSSNER (*Biochem. Z.*, 1923, 135, 183—216).—A critical review of the whole of the available literature on the occurrence of malic acid in plants leads to the conclusion that, contrary to general opinion, the wide distribution of malic acid is untenable. The proof of the identity of this acid is insufficient in numerous cases. H. K.

**Identity of the Sugar Extracted from the Manna of the Carob Tree with Pinitol or Methyl-d-inositol.** C. CHAUAUX (*Bull. Soc. Chim. biol.*, 1922, 4, 597—600).—An exudation found on the trunk of the carob tree (*Ceratonia siliqua*, L.) yielded 84% of pinitol when extracted with alcohol. E. S.

**The Prolamine of *Coix lacryma*, L.** GISABURO HATTORI and SHIGERU KOMATSU (*J. Biochem. [Japan]*, 1922, 1, 365—369).—Kernels of *Coix lacryma*, L., gave: Water 12.33, ash 7.06, protein nitrogen 2.92, crude protein 18.68, crude starch 50.66, soluble non-nitrogenous matter 4.93, crude fat 4.69, and crude fibre 7.42%. Coicine was prepared by extracting the meal with 80% alcohol at 78° and after further purification formed a yellowish-brown powder containing 0.6% of ash. The distribution of nitrogen in the pure prolamine was determined by the method of Osborne and Harris (*J. Amer. Chem. Soc.*, 1903, 22, 323) as follows: Humin nitrogen 0.1%, ammonia nitrogen 3.32%, basic nitrogen 0.94%, non-basic nitrogen 0.23%, monoamino-nitrogen 5.50%, imino-nitrogen 6.95%, total nitrogen 16.84. Determinations of the amino-acids gave glutamic acid 20.65%, leucine 4.10%, tyrosine 1.46%, arginine 0.20%, histidine 1.88%, and lysine 0.76%. K. K.

**The Influence of Hexamethylenetetramine and Formaldehyde on the Internal Morphology and the Chemistry of the Haricot Bean.** E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1923, 176, 404—407).—Both hexamethylenetetramine and formaldehyde in small doses are nutrients for the haricot bean. They cause, not only an increase in the weight of the plant (cf. this vol., i, 77) and a great development of leaf surface, but they are used, in addition,

for the differentiation and even lignification of the wood and of the pericycle, as well as for the formation of starch. W. G.

**The Changed Content of Urea in the Ripening of the Fruit of *Lycoperdon*.** NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 135, 1—20).—During ripening of *Lycoperdon gemmatum* (Puff-ball) there is a disappearance of carbohydrate (trehalose) and accumulation of nitrogen from 7.1 to 8.7%. The urea content increases during ripening, but disappears from the spores. The urea appears to be in the combined state, as it is not extracted by alcohol in an extractor, but is so by hot water. The urea probably functions as a reserve substance for the synthesis of arginine and purine bases, and for the production of ammonia used in building up tissue. H. K.

**Microchemical Researches on Coumarin.** ALBERT NAVEZ (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 159—173).—From the fact that tannins can be localised by microchemical methods in *Melilotus albus* and *M. altissimus* in the same regions as the glucoside discovered by Bourquelot and Hérissé (A., 1920, i, 586), it is considered likely that the glucoside (coumarigenin), which is derived from dextrose and coumarin hydrocoumarate, is combined, in the plant, with a second glucoside, melilotannic acid, derived from melilotic acid and tannin. E. E. T.

**Quantitative Composition of Coniferous Wood.** ASTRID CLEVE VON EULER (*Cellulosechem.*, 1923, 4, 1—11).—The mineral constituents, the protein, and the fat-resin components are regarded as not belonging to the true wood substance, and the analytical results are calculated, with the exclusion of these, in terms of carbohydrates and lignin. To the lignin belongs the so-called "alcohol resin," which is regarded as a lignin derivative soluble in alcohol. This is estimated, after removal of the fat and oleo-resin by extraction for six hours in benzene, by a further extraction with 96% alcohol for twenty-four hours. It is extracted very slowly, and the dried alcoholic extract is not completely soluble in alcohol. In the estimation of the lignin by hydrolysis of the carbohydrates with 72% sulphuric acid, the result is always higher than when 40% hydrochloric acid is used, owing to the combination of sulphuric acid groups with the lignin. A correction of 5.7 units should be deducted from the lignin value found by the sulphuric acid method. By both methods, the acetyl group is eliminated from the lignin as the result of hydrolysis, and this is compensated by adding 2.0 units to the percentage of lignin found. All results are then calculated in terms of the pure wood substance, the "alcohol resin" being added to the insoluble lignin under the designation of lignin soluble in alcohol. The lignin value of the wood is not a specific constant, but varies within limits according to the origin of the sample. Recalculated on the above principle, the analysis published by Klason in 1921 becomes: Cellulose, 54.10; hemicelluloses comprising hexosans, 3.06, and pentosans 12.25; total carbohydrates, 69.40%; lignin, including the acetyl group, 30.60%. J. F. B.

## Organic Chemistry.

**The Pyridine Extract of Upper Silesian Coal : Preliminary results.** II. F. HOFMANN and P. DAMM (*Brenstoff-Chem.*, 1923, 4, 65—73; *ibid.*, 1922, 3, 73).—In the fraction of the "neutral oil" boiling above  $300^{\circ}$  at ordinary pressures, paraffins, other saturated hydrocarbons, and unsaturated hydrocarbons were found to be present. The first were for the most part separated by treatment with acetone in which they were much the least soluble. The last two could not be satisfactorily separated by liquid sulphur dioxide, but were so by means of methyl alcohol, in which the unsaturated hydrocarbons alone were soluble. The insoluble saturated hydrocarbons were treated with acetone at  $0^{\circ}$  and at  $-18^{\circ}$  to separate any paraffins still present. Five hundred kg. of coal gave 42 kg. of pyridine extract containing 82 g. of paraffins, 332 g. of other saturated hydrocarbons, and 769 g. of unsaturated hydrocarbons. All the hydrocarbons were purified by recrystallisation and distillation at low pressures, alone and over sodium in a current of carbon dioxide. The unsaturated hydrocarbons received, in addition, treatment with methyl sulphate in which they were soluble.

There were identified in the paraffinoid portion: the hydrocarbons  $C_{21}H_{44}$  to  $C_{27}H_{56}$  inclusive. Evidence was obtained that a hydrocarbon separated by Pictet (A., 1916, i, 800) from a benzene extract of a coal, which he identified with Brodie's melene, was probably a mixture of the above paraffins. The other saturated hydrocarbons present appeared to be  $C_{17}H_{36}$ ,  $C_{17}H_{28}$ ,  $C_{18}H_{28}$ ,  $C_{19}H_{30}$ ,  $C_{22}H_{38}$ ,  $C_{23}H_{38}$ , and  $C_{24}H_{40}$ , but these formulæ are given with reserve owing to the difficulty of deducing definitely the number of hydrogen atoms present in a molecule of these hydrocarbons from the analytical figures. They are probably partly reduced and partly substituted polynuclear aromatic hydrocarbons.

The unsaturated hydrocarbons were also difficult to place, determinations of the refractive index giving no satisfactory aid. The following appeared to be present:  $C_{18}H_{20}$  (a partly reduced and alkyl-substituted naphthalene derivative),  $C_{16}H_{20}$ ,  $C_{17}H_{22}$ ,  $C_{18}H_{22}$ ,  $C_{19}H_{24}$  (partly reduced and substituted anthracene and phenanthrene, etc., derivatives),  $C_{21}H_{26}$  (a partly reduced and substituted tetranuclear derivative. Methylanthracene,  $C_{15}H_{12}$ , was definitely isolated among these hydrocarbons. T. S. W.

**The Preparation of True Acetylene Hydrocarbons.** M. BOREGUEL (*Compt. rend.*, 1923, 176, 751—753).—The difficulties encountered in the preparation of pure acetylenes by the action of potassium or sodium hydroxide on halogen derivatives of saturated hydrocarbons are largely avoided by eliminating the hydrogen halide by means of finely powdered sodamide suspended in benzene or xylene. No isomerisation or polymerisation occurs, and the

true acetylene hydrocarbon is almost the sole product owing to the automatic formation of the sodium derivative, which after removal of the diluent is decomposed by the addition of ice and a mineral acid. The preparation of *n*-pentinene,  $C_5H_7 \cdot CH_2 \cdot C \equiv CH$ , b. p.  $39.6-40^\circ$ , and of  $\gamma$ -phenylpropinene,  $C_6H_5 \cdot CH_2 \cdot C \equiv CH$ , b. p.  $69.5-70^\circ/18$  mm., by this method is described, and also of methyl propargyl ether,  $CH_3 \cdot O \cdot CH_2 \cdot C \equiv CH$ , b. p.  $63^\circ$ , from  $\beta$ -dibromopropyl methyl ether, and ethyl propargyl ether,  $C_2H_5 \cdot O \cdot CH_2 \cdot C \equiv CH$ , b. p.  $79.5-80^\circ$ , from the corresponding dibromopropyl ethyl ether. Phenylacetylene was obtained in a pure condition, b. p.  $140.5-141^\circ$ , from styrene dibromide and sodamide. G. F. M.

**Spinacene : its Oxidation and Decomposition.** A. CHASTON CHAPMAN (T., 1923, 123, 769-779).

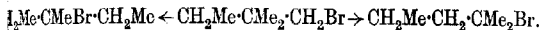
**Compounds of Aluminium Bromide with Phosphorus Bromides and Organic Bromides.** V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1891-1896).—A compound,  $AlBr_3 \cdot PBr_5 \cdot EtBr$ , is obtained by the addition with cooling of a solution of phosphorus pentabromide in ethyl bromide to a similar solution of aluminium bromide. This compound is, unlike its constituents, stable above  $150^\circ$ , decomposition occurring at  $230^\circ$ , with evolution of hydrogen bromide and formation of some pentabromoethane. The complex is immediately decomposed by water, in which it is completely soluble, and the entire bromine content may be precipitated by silver nitrate, ethyl alcohol being identifiable in the solution. A similar compound,  $AlBr_3 \cdot PBr_5 \cdot EtBr$ , m. p.  $160^\circ$  (decomp.), may be obtained by substituting phosphorus tribromide for the pentabromide in the above reaction, whilst a third compound,  $AlBr_3 \cdot PBr_3 \cdot CMeBr_2$ , m. p.  $134^\circ$ , may be obtained by substituting ethylidene dibromide for ethyl bromide. Aluminium bromide and phosphorus pentabromide, if mixed in carbon disulphide solution, form a compound,  $AlBr_3 \cdot PBr_5$ , decomposing at  $100^\circ$ . R. T.

**The Structure of Complex Compounds.** V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1896-1905).—The structure of complexes of ethyl bromide with the bromides of aluminium and phosphorus, such as  $AlBr_3 \cdot PBr_5 \cdot EtBr$  (preceding abstract), is discussed. The combination of molecules to form complexes is explained as being due to the action of electrons contained in the various atoms of the molecule, and the molecules combined together to form a complex exert a profound influence on each other. The result of this is to increase the reactivity of these groups, and, if molecules of water enter the complex, hydrolysis of its constituents takes place with abnormal rapidity and completeness. R. T.

**The Isomeric Transformations of Halides of Alcohols, and of Sulphovinic Acids leading to the Regrouping of Carbon Atoms.** A. E. FAVORSKI (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 43-80).—Various examples of intramolecular rearrangement of organic compounds are studied, in particular those of halogen derivatives of hydrocarbons. From these, it is concluded that a

dition of strain may exist between carbon-carbon linkings, which may, in favourable circumstances, lead to dissociation. This tendency is weakest with triple linkings, and strongest with single ones. For saturated compounds, it is most marked in cyclic groupings, and with open-chain compounds between quaternary carbon atoms, i.e., those joined to four others, as in tetraphenylmethane or hexaphenylethane. Tertiary carbon atoms joined to other atoms multiply bound, will often undergo rearrangement, leading to the transposition of radicles. The mobility of radicles attached to tertiary carbon atoms depends, not only on the condition of strain of the bonds, but also on the degree of interaction between the radicles themselves.

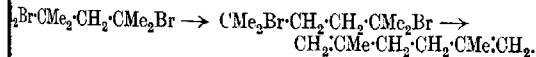
[With NADESHDA SAKARA.]—The acetate of  $\beta\beta$ -dimethylbutyl alcohol has b. p.  $152^{\circ}$ – $153^{\circ}$  at 755 mm., and its phenylurethane, m. p.  $65^{\circ}$ – $66^{\circ}$ . When oxidised, the alcohol yields small quantities of  $\alpha\alpha$ -dimethylbutaldehyde, b. p.  $102^{\circ}$ – $104^{\circ}$ , and of  $\alpha\alpha$ -dimethylacrylic acid, b. p.  $186^{\circ}$ – $187^{\circ}$ /755 mm., m. p.  $-13^{\circ}$ .  $\alpha$ -Bromo- $\beta$ -dimethylbutane, b. p.  $83^{\circ}$ – $85^{\circ}$ /145 mm.,  $d_4^{20}$  1.1958, prepared by treating the alcohol in a sealed tube at  $100^{\circ}$  with hydrogen bromide, undergoes isomeric change, which may occur in the following ways:



In order to decide which of these is produced,  $\gamma$ -bromo- $\gamma$ -methylpentane, b. p.  $82^{\circ}$ – $83^{\circ}$ /145 mm.,  $d_4^{20}$  1.2066,  $R_d = 37.67$ , is synthesised by the action of hydrogen bromide on the product of the interaction of magnesium ethyl bromide with ethyl acetate. The other,  $\beta$ -bromo- $\beta$ -methylpentane, b. p.  $77^{\circ}$ – $78^{\circ}$ /145 mm.,  $d_4^{20}$  1.1807,  $R_d = 37.67$ , is obtained in a similar way from the product of the interaction between magnesium propyl bromide and acetone. It is hence concluded that the action of hydrogen bromide on the alcohol is to produce  $\gamma$ -bromo- $\gamma$ -methylpentane. Alcoholic alkali hydroxide acts on it, to produce a mixture of hexenes as follows:  $\text{CH}_2\text{Me.CMe.CHMe.CH}_2\text{Me.CMeBr.CH}_2\text{Me} \rightarrow \text{CH}_2\text{Me.C(CH}_3)_2\text{.CH}_2\text{Me.}$

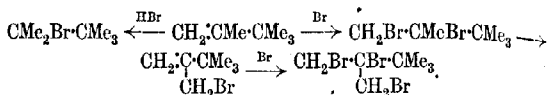
The first of these is the main product,  $\gamma$ -methylpentene being present only in very small quantity.

[With N. SHIBAEV.]— $\alpha\delta$ -Dibromo- $\beta\beta\delta$ -trimethylpentane, under the influence of diethylamine, is transformed into diisobutenyl in the following way:



With EUGÉNIE OPEL.]— $\beta\gamma\gamma$ -Trimethyl- $\Delta^4$ -butene, b. p.  $75^{\circ}$ – $80^{\circ}$ , prepared from  $\beta$ -hydroxy- $\beta\gamma\gamma$ -trimethylbutane by distillation through 50% sulphuric acid. When oxidised, it yields  $\beta\gamma\gamma$ -trimethyl- $\alpha\omega$ -diol, m. p.  $91^{\circ}$ – $92^{\circ}$ , which on further oxidation yields hydroxy- $\alpha\beta\beta$ -trimethylbutyric acid, m. p.  $104^{\circ}$ – $106^{\circ}$ , and finally dimethylpropionic acid and formic acid. The hydrocarbon, on oxidation in ethereal solution, gives a dibromide,  $\text{C}_7\text{H}_{14}\text{Br}_2$ , m. p.  $38^{\circ}$ – $39^{\circ}$ , from which it is regenerated on distillation from potassium dust. Bromination in acetic acid solution gives the bromide

of  $\beta$ -bromo- $\beta$ - $\gamma$ -trimethylbutane, m. p. 150—151°, which on hydrolysis yields the same alcohol, so that bromination does not appear to cause any structural change. Bromination in ethereal solution also produces small quantities of a tribromide,  $C_7H_{13}Br_3$ , m. p. 50.5—52°, and of saturated and unsaturated monobromides. The formation of these is explained by the following scheme:



The dibromide, when heated for eight hours at 160° in a sealed tube with sodium ethoxide, gives a mixture of a hydrocarbon and a mixture of ethers, b. p. 145—148°. The hydrocarbon on oxidation gives a mixture of  $\alpha$ -dimethylpropionic, formic, and  $\beta$ -dimethylbutyric acids, which points to it being  $\delta$ -dimethyl- $\Delta^4$ -pentadiene, b. p. 80—83°. This, when heated in a sealed tube at 100° with sodium, is converted into sodio- $\delta$ -dimethyl- $\Delta^4$ -pentene, which can be converted by the action of carbon dioxide into the sodium salt of  $\delta$ -dimethyl- $\Delta^4$ -pentene- $\alpha$ -carboxylic acid. The free acid has m. p. 48—49.5°. The ether, b. p. 145—148°, is a mixture of two isomeric ethers,  $CMe_3 \cdot CMe \cdot CH \cdot OEt$  and  $CMe_3 \cdot C(CH_2) \cdot CH_2 \cdot OEt$ , whilst the hydrocarbon is formed by an intramolecular rearrangement:  $CH_2 \cdot C(CH_2Br) \cdot CMe_3 \rightarrow CH_2 \cdot CBr \cdot CH_2 \cdot CMe_3 \rightarrow CH_2 \cdot C \cdot CH \cdot CMe_3$ .

[With SERGEI KAROLEV.]— $\beta$ - $\beta$ -Diphenylpropane- $\alpha$ -ol, b. p. 186—187°/15 mm.,  $d_4^{20}$  1.0968, is prepared by the reduction of  $\alpha$ -diphenylpropaldehyde; the urethane has m. p. 148—149°, and the acetate, b. p. 182—183°/14 mm. Dehydration with potassium sulphate caused intramolecular rearrangement, with the production of  $\alpha$ -diphenylpropylene,  $CH_3 \cdot CPh_2 \cdot CH_2 \cdot OH \rightarrow CH_3 \cdot Ph \cdot C \cdot CHPh$ .

R. T.

**Catalytic Dehydration of Alcohols by Dilute Sulphuric Acid.** J. B. SENDRENS (*Compt. rend.*, 1923, 176, 813—816).—The dehydration of alcohols by sulphuric acid does not consist in a simple absorption of water, but is a catalytic action, and the large proportion or high concentration of acid required for the dehydration of certain alcohols is only for the purpose of raising the temperature to an extent sufficient for the catalytic reaction to proceed, and, as would be expected from this reasoning, the same results are obtained with either concentrated or diluted sulphuric acid, provided the proportions of acid and alcohol employed are such as to produce a reaction mixture of the same boiling point in each case. With propyl alcohol, for example, a mixture of 100 c.c. of alcohol and 75 c.c. of concentrated sulphuric acid boils at about 140°, and gives propylene almost exclusively, whilst 40 c.c. of acid gives a mixture boiling at 125°, and a yield of 30% of propyl ether is obtained with the propylene. Propyl alcohol with 200% of the dihydrate,  $H_2SO_4 \cdot 2H_2O$ , also gives a mixture boiling at about 135°, with propylene as the chief product, and with 60% of

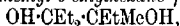
he dihydrate the b. p. is  $125^{\circ}$ , and 38% of propyl ether is produced. A reaction mixture boiling at  $125^{\circ}$  is also obtained with the hydrate,  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , mixed with a third of its volume of propyl alcohol, and the product consists of 40% of propyl ether, and a correspondingly diminished amount of propylene. Precisely analogous results were obtained with ethyl, isopropyl butyl, isobutyl, and isoamyl alcohols, the proportions of acid required to produce a certain result diminishing as the molecular weights and boiling points of the alcohols increase. Thus only a tenth of the quantity of  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  is required for the same volume of isoamyl alcohol as of propyl alcohol in order to produce the corresponding ether.

G. F. M.

**Preparation of Absolute Alcohol with Calcium Chloride and Lime.** WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1923, 45, 37—862).—An apparatus is described by means of which alcohol of 99.0—99.5% concentration may be prepared rapidly by the use of calcium chloride. An apparatus is also described for preparing absolute alcohol with lime. When absolute alcohol is distilled from an excess of lime, a little calcium is carried over, probably as calcium ethoxide. Metallic sodium is not suitable for the preparation of absolute alcohol, because (1) sodium ethoxide, alcohol, water, and sodium hydroxide form an equilibrium such that some water will always pass over with the alcohol, (2) sodium ethoxide is very sensitive to oxidation on exposure to the air. On distilling a concentrated alcoholic solution containing equimolecular proportions of water and calcium chloride, alcohol of 99.5% concentration, or stronger, passes over; on concentration of such a solution, a solid alcoholate, not a hydrate, separates when the boiling point reaches  $95$ — $100^{\circ}$ , and there is an equilibrium between the alcoholate and the hydrate present.

W. S. N.

**The Preparation of Various Pinacones by the Action of Frignard Reagents on  $\alpha$ -Hydroxymethyl Ketones.** R. JOUQUIN and SUNG WOUSENG (*Compt. rend.*, 1923, 176, 682—84).—Pinacones of the general type,  $\text{OH}\cdot\text{CRR}'\cdot\text{CR}''\cdot\text{Me}\cdot\text{OH}$ , where  $\text{R}$ ,  $\text{R}'$ , and  $\text{R}''$  are alkyl groups, are obtained by the action of magnesium alkyl iodides on  $\alpha$ -hydroxyl methyl ketones of the general formula  $\text{OH}\cdot\text{CRR}'\cdot\text{CO}\cdot\text{CH}_3$ , the preparation of which has been previously described (this vol., i, 302). Thus the interaction of 3 mols. of magnesium ethyl iodide on methyl  $\alpha$ -hydroxy- $\alpha$ -ethyl-propyl ketone gave  $\beta$ -methyl- $\delta$ -ethylhexane- $\gamma\delta$ -diol,



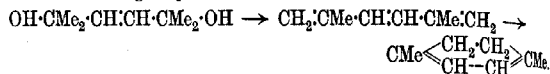
b. p.  $103$ — $104^{\circ}/11$  mm. From methyl  $\alpha$ -hydroxy- $\alpha$ -propylbutyl ketone and magnesium methyl iodide  $\beta$ -methyl- $\gamma$ -propylhexane- $\gamma\delta$ -diol,  $\text{OH}\cdot\text{CPr}_2\cdot\text{CMe}_2\cdot\text{OH}$ , b. p.  $110$ — $112^{\circ}/12$  mm., was obtained, whilst the same hydroxy-ketone and magnesium propyl iodide gave  $\alpha$ -methyl- $\epsilon$ -propyloctane- $\delta\epsilon$ -diol, b. p.  $137$ — $140^{\circ}/19$  mm. Magnesium methyl iodide and methyl  $\alpha$ -hydroxyl- $\alpha$ -tert.-butylethyl ketone gave  $\beta\gamma\delta$ -tetramethylpentane- $\gamma\delta$ -diol,  $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$ , b. p.  $99$ — $100^{\circ}/13$  mm. All these pinacones are viscous liquids or low-melting solids. They have no characteristic odour, and do

not furnish crystalline hydrates with water. On dehydration by heating with dilute mineral acids, they are converted into pinacolines.  
G. F. M.

**Addition of Hydrogen to Acetylene Derivatives.** VIII. I. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1830—1848).—When  $\beta$ -dimethylhexene- $\beta$ -diol is reduced with hydrogen by the Sabatier process, using a palladium catalyst, two stereoisomeric ethylenic reduction products may be obtained, namely, the *cis*- and *trans*-isomerides of  $\beta$ -dimethyl- $\Delta^7$ -hexene- $\beta$ -diol,  

$$\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{OH}.$$

One isomeride, the  $\alpha$ -form, melts at  $76\cdot5$ — $77^\circ$ , whilst the  $\beta$ -isomeride has m. p.  $69$ — $69\cdot5^\circ$ . The dehydration of these substances by sulphuric acid leads to the production of 2:3-dihydro-*p*-xylene in the following way:



The two isomerides are not interconvertible under the conditions of the catalytic reduction, but are formed side by side, the quantity of each isomeride in the reaction product being determined by the velocity with which the reduction is conducted. Thus if a large quantity of catalyst is used, the reduction proceeds rapidly to completion, giving as the main product the  $\alpha$ -isomeride, whilst a slow reduction produces principally the  $\beta$ -form. Both isomerides are converted by heat or by mild dehydrating agents into the  $\gamma$ -lactone, the  $\alpha$ -form suffering dehydration more readily. With phosphorus tribromide, they give an oily, unsaturated monobromide,  $\text{C}_8\text{H}_{13}\text{Br}$ . Bromination of the isomerides gives for each an oil and a crystalline compound, m. p.  $98\cdot5$ — $99\cdot5^\circ$ , both having the formula  $\text{C}_8\text{H}_{15}\text{O}_2\text{Br}_2$ . From the  $\alpha$ -isomeride, the main product is the oil, which is obtained as a by-product from the bromination of the second form. It is probable that some conversion of the stereoisomerides is effected in each case by the hydrogen bromide liberated during bromination.  
R. T.

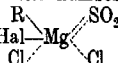
**Existence of Alkyl Chlorites.** GIORGIO RENATO LEVI (*Gazzetta*, 1923, 53, i, 40—42).—Attempts to prepare alkyl chlorites from either silver chlorite and ethyl halide or barium chlorite and methyl sulphate have proved unsuccessful, an explosive reaction usually taking place (cf. A., 1922, i, 527; ii, 567).  
T. H. P.

**Phosphorous Acid Esters.** The Influence of the Character of the Groups  $\text{R}'$ ,  $\text{R}''$ ,  $\text{R}'''$  on the Stability of the Molecular Complexes  $\text{R}'\text{R}''\text{R}'''\text{C}\cdot\text{O}\cdot\text{PCl}_2$  and  $\text{R}'\text{R}''\text{R}'''\text{C}\cdot\text{O}\cdot\text{P}(\text{OH})_2$ . I. DAVID RUNCIMAN BOYD and GUY CHIGNELL (*T.*, 1923, 123, 813—817).

**The Action of Organomagnesium Salts on Sulphuryl Chloride; Preparation of Aliphatic Sulphonyl Chlorides and Bromides.** E. CHERBULEZ and O. SCHNAUDER (*Helv. Chim. Acta*, 1923, 6, 249—257).—By the action of aromatic or aliphatic

organomagnesium compounds on sulphuryl chloride, sulphonyl chlorides or bromides can be obtained, provided that the solution of the Grignard compound is added to the sulphuryl chloride, the latter being present in excess throughout the reaction. In the aromatic series, the yields are poor, but in the aliphatic series they are from 25% to 35% of theory. The yields are lower at very low temperatures,  $-20^{\circ}$  to  $-40^{\circ}$ , at which the product is chiefly halogenated hydrocarbon, than at higher temperatures; the best yields of aliphatic sulphonyl compounds are obtained at  $+10^{\circ}$ . Magnesium benzyl chloride behaves as an aliphatic compound. The magnesium alkyl chlorides and iodides with sulphuryl chloride both give sulphonyl chlorides, but the magnesium alkyl bromides give sulphonyl bromides, which are new. *Methanesulphonyl bromide*, obtained in 21% yield from methyl bromide, is a colourless liquid with a pungent odour, b. p.  $72-73^{\circ}/15$  mm., or  $173^{\circ}$  (decomp.) at the ordinary pressure. *Ethanesulphonyl bromide* (35% yield), from ethyl bromide, a colourless liquid with a pungent odour, has b. p.  $80^{\circ}$  at 13 mm., or  $170^{\circ}$  with rapid decomposition at the ordinary pressure.

The course of this reaction can be best explained by Meisenheimer and Casper's theory of the constitution of organomagnesium compounds (A., 1921, i, 654), in which it is assumed that they are co-ordination compounds. Assuming the co-ordination number of magnesium to be 6, the intermediate compound



may be formed. In favour of the formation of such an intermediate compound is the observation that, at low temperatures, when an iodide is used, the precipitation of the salt  $\text{MgCl}_2$  takes place very slowly. Such an intermediate compound would explain the formation of  $\text{R}\cdot\text{SO}_2\text{Cl}$  or  $\text{R}\cdot\text{SO}_2\text{Hal}$ , according to the nature of the halogen. When this is bromine, in the aliphatic series  $\text{R}\cdot\text{SO}_2\text{Br}$  is formed exclusively, but in the aromatic series a mixture of  $\text{R}\cdot\text{SO}_2\text{Br}$  and  $\text{R}\cdot\text{SO}_2\text{Cl}$  is obtained. At very low temperatures, a mixture of  $\text{R}\cdot\text{Br}$  and  $\text{R}\cdot\text{Cl}$  is formed. The formation of sulphinic acid and sulphone by the action of an organomagnesium compound on a sulphonyl chloride can be explained by the same hypothesis.

In the course of the reaction between organomagnesium bromides or iodides and sulphuryl chloride, free bromine or iodine is always formed, the proportion increasing at higher temperatures.

E. H. R.

**Hydration of Acetic and Hydrochloric Acids and the Factors Determining the Activity of the Hydrogen-ion.** W. C. McC. LEWIS, DORIS E. MERRIMAN, and T. MORAN (*J. Amer. Chem. Soc.*, 1923, 45, 702-712).—The activity of the hydrogen-ion (produced from acetic acid) in the presence of various amounts of sucrose has been experimentally determined at  $30^{\circ}$ . In the case of acetic acid, the activity of the hydrogen-ion can be completely accounted for by assuming acetic acid to be hydrated to the extent of three molecules of water for each molecule of acid,

and then identifying activity with the concentration of the hydrogen-ion per unit of free water space in the sucrose solution. The change in the activity of the hydrogen-ion (produced from hydrochloric acid) in the presence of sucrose cannot be accounted for by a space correction alone. In this case, the heat of dilution of the ion must be considered, and it is shown that by combining the two above factors it is possible to account for 80–90% of the observed activity; no definite conclusion is drawn as to the causes of the excess activity observed. It is pointed out, however, that the excess might be attributed to an increased ionisation of the acid, a modification of a suggestion originally made by Scatchard (A., 1922, i, 230). The average degree of hydration of hydrogen chloride in solution between 0.1N and 1.2N has been calculated by an examination of the kinetics of the inversion of sucrose by this acid, employing the data of Fales and Morrell (A., 1922, ii, 832). It is shown to be approximately 7. J. F. S.

**Electrolysis of Acetic Acid with Commutated Direct Current.** EMIL BAUR (*Z. Elektrochem.*, 1923, 29, 105–110).—Solutions of acetic acid of various concentrations and also solutions of potassium acetate in acetic acid have been electrolysed between bright platinum electrodes by means of commutated direct current. The products of electrolysis consist of carbon dioxide and hydrocarbons, the latter consisting of approximately equal volumes of ethane and methane. The results are discussed in connexion with the author's hypothesis of the optically sensitised photolysis.

J. F. S.

**Separation of Methyl Oleate and Linoleate by Fractional Distillation.** ÉMILE ANDRÉ (*Compt. rend.*, 1923, 176, 686–689).—The separation by fractional distillation under pressures of 1–3 mm. of mixtures of methyl oleate and linoleate was attempted, but the polymerisation which occurred during the long series of repeated distillations that was necessary proved a serious obstacle against the isolation of the higher boiling methyl linoleate in a pure condition. The highest iodine value obtained was 160, as compared with 172.7 for the pure ester. A certain quantity of fairly pure methyl oleate was, however, obtained having an iodine value of 92–95, by uniting the fractions with the lowest iodine values and redistilling. It is suggested that the addition of a small quantity of a phenolic substance (antioxygen) to the esters might facilitate the separation.

G. F. M.

**The Course of the Reaction in the Acetoacetic Ester Synthesis.** K. H. MEYER (*Z. angew. Chem.*, 1923, 36, 169).—Scheibler's view (*ibid.*, 6; cf. also this vol., i, 82) that, in the above synthesis, ethyl sodioacetate is first formed and reacts with a second molecule of ethyl acetate to give a salt-like condensation product, which is then decomposed by acids into alcohol and ethyl acetoacetate, was put forward by the author ten years ago (*Annalen*, 1913, 398, 49). Whilst in the latter case the explanation was based on analogy with ethyl sodiomalonate, Scheibler's work appears to afford experimental proof of it.

W. T. K. B.

**Action of the Grignard Reagent on Keto-acids.** PHILIP K. PORTER (*J. Amer. Chem. Soc.*, 1923, 45, 1086—1087).—Lævulic acid reacts in ethereal solution with magnesium methyl iodide to give isohexolactone, and with magnesium ethyl bromide to give the lactone of  $\gamma$ -hydroxy- $\gamma$ -methylhexoic acid, the yields being 31.5% and 35.1%, respectively. The yields of these compounds previously obtained, starting from ethyl lævulate, are 30—35% (Noyes and Marvel, A., 1917, i, 455) and 35% (Grignard and Moissan, A., 1903, i, 31), respectively. W. S. N.

**The Hydroxy-acids Contained in an Oil from Grape Stones.** ÉMILE ANDRÉ (*Compt. rend.*, 1923, 176, 843—845).—The hydroxy-acids, the presence of which in oil of grape stones has previously been established (*ibid.*, 1921, 172, 1296), were isolated from the other fatty acids which accompanied them by taking advantage of the partial insolubility of the hydroxy-acids in light petroleum when a relatively high proportion is present in the fatty acid mixture, and, secondly, of the greater solubility of the lithium salts of the hydroxy-acids, which results in their accumulating in the mother-liquors from the crystallisation of the lithium soap. By repeated alternate application of these two principles, 15—16% of the original material was separated as a viscous liquid, having saponification value 222, iodine value 69.2, and average molecular weight 252.2. It is concluded that the acetyl value of the oil of grape stones cannot therefore be attributed to ricinoleic acid, but rather to hydroxy-acids of lower molecular weight containing  $C_{14}$  to  $C_{16}$ . There would appear to be at least two such hydroxy-acids, one saturated, and the other having an ethylenic linking.

G. F. M.

**Synthesis of an Acid of the Digitoxonic Acid Group.** GÉZA ZEMPLEN (*Ber.*, 1923, 56, [B], 686—689).—An acid which closely resembles natural digitoxonic acid in structure and properties has been obtained by the condensation of crotonaldehyde with ethyl bromoacetate and oxidation of the product with perbenzoic acid.

*Ethyl  $\beta$ -hydroxy- $\Delta^1$ -hexenoate*,  $CHMe:CH-CH(OH):CH_2 \cdot CO_2Et$ , b. p.  $86^\circ/0.5$  mm., is prepared by the addition of activated zinc to a well-cooled mixture of crotonaldehyde and ethyl bromoacetate. The success of the operation (which is fully described in the original) appears to be greatly dependent on details; replacement of zinc by magnesium leads to less satisfactory results. The ester is oxidised by perbenzoic acid in chloroform solution, and the product converted by barium hydroxide into *barium  $\beta,\delta$ -trihydroxy- $n$ -hexoate*, which could not be caused to crystallise. The corresponding free acid does not exhibit any tendency towards crystallisation; it yields a *hydrazide*,  $C_{12}H_{18}O_4N_2$ , coarse, colourless crystals, m. p.  $159^\circ$ . H. W.

**Preparation of Oxalic Acid from Acetylene.** M. LUCRETIA KEARNS, L. HEISER, and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1923, 45, 795—799).—Oxalic acid can be prepared by passing

acetylene into dilute nitric acid (75% by volume), with mercuric nitrate as catalyst. An acetylene-mercury compound is first formed, which gives acetaldehyde with part of the nitric acid; the aldehyde is then oxidised to oxalic acid by the nitric acid. Oxalic acid is also formed by the action of (1) nitrogen oxides on acetylene, (2) nitrogen oxides on acetaldehyde, (3) acetaldehyde vapour on nitric acid.

Acetaldehyde can be obtained by passing (1) acetylene over dry mercuric nitrate, (2) nitrogen oxides over metallic mercury, and then passing acetylene over the resulting salt. The mercury salt may be regenerated, after reduction, by means of nitrogen oxides.

W. S. N.

**The Decomposition of the Peroxides of Succinic, Fumaric, and Benzoic Acids by Heat and their Relation to the Behaviour of the Corresponding Salts on Electrolysis.** FR. FICHTER and ALBERT FRITSCH (*Helv. Chim. Acta*, 1923, 6, 329-336).—In a previous paper (A., 1918, i, 369), it was suggested that in the Kolbe hydrocarbon synthesis by the electrolysis of salts of organic acids, unstable peroxides are formed intermediately and are decomposed by the relatively high temperature of the anode, forming the hydrocarbon. Confirmation of the theory is obtained from a study of the decomposition of peroxides of succinic, fumaric, and benzoic acids. Succinyl peroxide (purity about 86%) decomposes explosively when heated in a bomb, forming a mixture of gases containing 55.2% of carbon dioxide and 21.1% of ethylene, the volume ratio being 2.6:1 instead of the theoretical 2:1. Gentler decomposition by heating in boiling xylene gave a ratio 2.25:1. Electrolysis of succinates gave a very similar ratio, 2.4:1. Fumaroyl peroxide could only be obtained in a very impure form by the action of sodium peroxide on fumaroyl chloride in ice-water. When decomposed in the bomb it gave 67.6% of the expected yield of carbon dioxide and 10.6% of acetylene. Electrolysis of sodium fumarate gave 19.9% of the theoretical yield of acetylene. Benzoyl peroxide decomposed explosively when heated in a bomb at 180–200°, giving 80.2% of the theoretical yield of carbon dioxide and 39.1% of diphenyl. By the electrolysis of benzoates, no diphenyl is produced, because the oxidation potential needed for peroxide formation is higher than the nucleus can carry without itself being oxidised (cf. Fichter and Krummenacher, *loc. cit.*).

E. H. R.

**Ketens. XLVI. Attempts to Prepare Diketens.** H. STAUDINGER and W. KREIS (*Helv. Chim. Acta*, 1923, 6, 321-326).—It was hoped to prepare the diketene  $\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CO}$  from ethanetetra-carboxylic dianhydride. This anhydride can be obtained by treating ethanetetra-carboxylic acid with an ethereal solution of oxalyl chloride, or by the action of oxalyl chloride on the silver salt, as well as by the method of Philippi and Hanusch (A., 1920, i, 594). When heated under reduced pressure, the anhydride gives no trace of ketene; with aniline, it gives a diamide which, when heated, decomposes into carbon dioxide and succin-

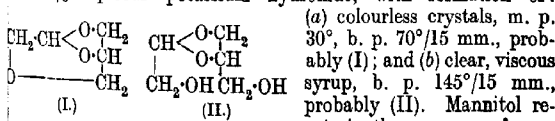
anilide. When ethylenetetracarboxylic acid is boiled for several days, a new acid is formed, which appears to be *ethylenetricarboxylic acid*, m. p. 180—184°.

With oxalyl chloride, the tetracarboxylic acid or its silver salt decomposes, forming a brown, amorphous compound, which appears to be a polymerised form of a new *carbon suboxide*, CO·C·C·CO. A similar brown, amorphous substance is formed, together with diphenylacetic anhydride, by the action of diphenylketen on ethylenetetracarboxylic acid. *Dimethyldicarboxyglutaric dianhydride* (annexed formula) was obtained by the action of diphenylketen in ethereal solution on dimethyldicarboxyglutaric acid. It forms colourless crystals, m. p. 126—127°. When heated, the anhydride decomposes without formation of any trace of diketene.

E. H. R.

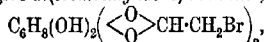
**Cellulose Chemistry. III. Bromoparacetaldehyde and Monobromoacetaldehyde. Preparation, Properties, and Utilisation for the Synthesis of Bromo- and Hydroxy-cyclic Acetals related to Polysaccharides.** HAROLD HIBBERT and HAROLD SANFORD HILL (*J. Amer. Chem. Soc.*, 1923, 45, 734—751).—Bromoparacetaldehyde (cf. Helferich and Speidel, A., 1922, i, 6), which is prepared by the addition of bromine to cold paracetaldehyde in the presence of sunlight, breaks down on slow distillation into bromoacetaldehyde (*semicarbazone*, long, flat needles, m. p. 128°, lecomp.), the polymerisation of which to the trimolecular compound occurs spontaneously, more rapidly in the presence of concentrated acids. The bromo-aldehyde has been used to prepare cyclic acetals, the essential structure of which is present in maltose, cellobiose, levoglucosan, diamylose, and the cellulose unit.

The cold, crude product of bromination of paracetaldehyde reacts with  $\alpha$ -bromohydrin, with formation of *bromoethylidene bromohydrin*, a heavy oil, b. p. 118—120°/10 mm., yield 56%, and with ethylene glycol with formation of *bromoethylidene glycol*, a heavy oil, b. p. 63—65°/12 mm.; the latter is also obtained in 12% yield when ethylene glycol is heated at 100° with a little sulphuric acid and the "crude syrup," obtained by extracting the crude bromination mixture by means of ether. Under similar conditions, trimethylene glycol reacts with the "crude syrup," yielding *bromoethylidene trimethylene ether*, b. p. 80—86°/12 mm. Similarly, glycerol, "crude syrup," and sulphuric acid give *bromoethylidene glycerol*, b. p. 137—140°/15 mm., alternative formulæ of which are suggested; this compound is decomposed by means of 3·5% aqueous potassium hydroxide, with formation of:



concentrated hydrochloric acid with cold, freshly distilled bromo-

acetaldehyde to give *di(bromoethylidene)-mannitol*,



slender, white needles, m. p. 137–141°, but this is not produced from either the extracted syrup or the crude bromination mixture. It is shown that acetaldehyde and  $\alpha$ -bromohydrin react in the presence of a trace of iodine to give *ethylidene bromohydrin*, a colourless oil, b. p. 168–169°.

W. S. N.

**The Preparation of Mesityl Oxide.** RENÉ LOCQUIN (*Ann. Chim.*, 1923, [ix], 19, 32–44).—A general survey of various methods shows that they may be grouped in two series, (a) those in which condensation and dehydration of two molecules of acetone are effected simultaneously, (b) those in which diacetone alcohol [*isohexane- $\beta$ -one- $\delta$ -ol*] is obtained as an intermediate. The author considers that a simple standard method is required, and gives details of one based on condensation under the influence of sodium hydroxide solution and subsequent dehydration by means of oxalic acid. Only 20% of the acetone reacts, and from this portion a 75% yield is obtained; the remainder may be recovered unchanged.

H. J. E.

#### Some Constitutional Problems of Carbohydrate Chemistry.

JAMES COLQUHOUN IRVINE (T., 1923, 123, 898–921).—A lecture delivered before the Chemical Society on February 22nd, 1923.

#### The Influence of some Normal Salts on the Mutarotation and Specific Rotation of Dextrose.

HANS MÜRSCHHAUSER (*Biochem. Z.*, 1923, 136, 66–70).—The velocity constants of the mutarotation of dextrose have been determined in the presence of a number of simple inorganic salts of the alkali and alkaline-earth metals and a few acetates in *N*-, 2*N*-, and 4*N*-concentrations of the salts. Of those examined, potassium chloride and bromide, like sodium chloride, retard the mutarotation, but hydrolysed salts of acetic acid accelerate it. The final value of the rotation of dextrose is influenced by the presence of salts, and twenty values are recorded ranging between  $[\alpha]_D +47.4$  and 61.2, the former for 4*N*-potassium iodide and the latter for 4*N*-calcium chloride.

H. K.

#### Physico-chemical Studies on Biological Reactions. III.

**Mutarotation of Sugars.** PAUL HIRSCH and ANNA ELISABETH KOSSUTH (*Fermentforsch.*, 1922, 6, 302–339).—The use of Löw's interferometer to follow the course of the mutarotation of dextrose and lactose shows that the refractive indices of solutions of these sugars prepared from the  $\alpha$ -modifications undergo slight increase in the refractive index, whilst those of solutions of the  $\beta$ -modifications show slight decrease, during the period of mutarotation (cf. Schmoeget, A., 1892, 948; Stolle, A., 1901, i, 368, 507; Trey, A., 1904, i, 292; Rabe, A., 1911, i, 14). These results throw doubt on Hudson's theory, that mutarotation of the sugars is due to hydration or dehydration.

Gradual increase in refractive index occurs also during the conversion of succinic anhydride into the acid, and during the

resolution of trimeric formaldehyde into simple molecules in aqueous solution; the results obtained in the latter case support Auerbach and Barschall's view that this resolution is accompanied by hydration (A., 1905, i, 859; 1908, i, 131). T. H. P.

**Fluoroacetyl Derivatives of Sugars.** I. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1923, 45, 833—835).—*Fluorotetra-acetylglucose*, m. p. 108°, *fluorohepta-acetylcellulose*, m. p. 187°, and *fluoro-riacetylxylose*, m. p. 87°, are prepared by the action of liquid hydrogen fluoride on the relevant acetyl sugar. The latter is placed in the receiver attached to a retort in which potassium hydrogen fluoride is heated. The operation takes thirty minutes. The methods of analysis are given. W. S. N.

**Dextrose and Sucrose Monosulphates.** V. T. SODA (*Biochem. Z.*, 1923, 135, 621—628; cf. A., 1922, i, 986).—By the action of chlorosulphonic acid in chloroform at  $-10^{\circ}$  on dextrose (18% excess) in dry pyridine, dextrose monosulphate is formed, and can be isolated without the intervention of the acetyl derivative. The solvents are removed, and the aqueous solution of the syrup suitably treated with lead oxide, barium carbonate, and silver sulphate to remove chlorides and sulphates. The crude barium salt is precipitated by alcohol. The pure brucine salt, crystallised from acetone, has m. p. 183° and  $[\alpha]_D^{25} -5.6$  (final value). The barium salt crystallises with  $2C_2H_5O$ ; the anhydrous salt has  $[\alpha]_D^{25} +32^{\circ}$ . In a similar manner, sucrose gives *barium sucrose monosulphate dihydrate*. The alcohol-free salt has  $[\alpha]_D^{25} +37.6^{\circ}$ . H. K.

**Mannose from White Spruce Cellulose.** E. C. SHERRARD and G. W. BLANCO (*J. Amer. Chem. Soc.*, 1923, 45, [4], 1008—1013).—Extraction of spruce wood flour by means of 2.8% sodium hydroxide solution gives no mannose, but the latter is formed when the alkali-extracted wood is hydrolysed by means of 5% hydrochloric acid. Moreover, an equal or even greater amount of dextrose is simultaneously produced, the total sugars formed being approximately equivalent to the cellulose removed. By the solution of cellulose in zinc chloride-hydrochloric acid solution or in Schweizer's reagent and reprecipitation, different amounts of mannose are removed. It is concluded that the mannose is not present as a mannan, and that either (1) if the mannose is not in true combination with the cellulose neither is part of the dextrose, or (2) both mannose and dextrose are loosely attached to the cellulose nucleus and hydrolyse with equal readiness. The latter alternative is probable, since mannose is found to be distributed in the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -portions of the cellulose. W. S. N.

**Attempts to Prepare Isomeric Osazones. Dimorphism of Two Hydrates of Galactose.** OLOF SVANBERG (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 25, 1—19).—Attempts to obtain a third ( $\gamma$ ) form of glucosazone and of glucosephenylmethylhydrazone were unsuccessful. Glucosephenylmethylhydrazone is converted by phenylhydrazine into glucosazone. All the specimens of glucosazone obtained, from whatever source, melted at about 204—206°.

(decomp.), and had initial  $[\alpha]_D -104 \pm 2^\circ$  in pyridine solution, showing weak mutarotation. Glucose- $\alpha$ -phenylhydrazone melts at about  $148^\circ$ , and has initial  $[\alpha]_D -87^\circ$  and final  $[\alpha]_D -53^\circ$  in aqueous pyridine. Its mutarotation was studied between  $p_H$  4.9 and 13.8, and was found to be accelerated both by alkalis and by acids. The m. p. of glucose- $\beta$ -phenylhydrazone was found to be  $115-116^\circ$ , a lower value than that given by Behrend (A., 1907, i, 481). The mutarotation of this substance is accelerated by acids and retarded by alkalis. In weak acid, the negative rotation increases very rapidly at first, then passing through the equilibrium values given by the  $\alpha$ -compound; the equilibrium solution probably contains the  $\gamma$ -form in addition.

Galactosephenylmethylhydrazone is converted by phenylhydrazine in pyridine-acetic acid solution into galactose-phenylhydrazone, the latter, in dilute acetic acid solution, being rapidly converted by phenylmethylhydrazone into the phenylmethylhydrazone. Galactosazone has initial  $[\alpha]_D +121 \pm 2^\circ$  in pyridine solution. Galactose-phenylhydrazone and -phenylmethylhydrazone (cf. Votoček, A., 1921, i, 544) both exhibit dimorphism, which (at any rate, in the former case) cannot be correlated with constitutional differences. The phenylhydrazone crystallises from hot solutions in leaflets, from cooler ones in needles, which change into leaflets on keeping. E. E. T.

**The Hydrolysis of Maltose by Extract of Malt.** L. MAQUENNE (*Compt. rend.*, 1923, 176, 804-806).—The reducing power of a preparation of malt extract to which maltose has been added increases in comparison with that of the malt alone up to a certain limit, which varies with the temperature. The maximum increase is attained at about  $50^\circ$ , whilst at  $60^\circ$  the increase is very small. These facts can be explained most naturally by the assumption that malt extract contains maltase in addition to amylase, and that the maltose is, by its action, partly hydrolysed to glucose. This observation will obviously throw doubt on the conclusions drawn from results obtained on the hydrolysis of starch by malt extract and based on the assumption that maltose was the sole product of hydrolysis (Maquenne and Roux, A., 1906, i, 327, 547; ii, 623). G. F. M.

**Carbohydrates. III. The Action of Phosphorus Pentachloride on Octa-acetylmaltose.** PERCY BRIGL and PAUL MISTELE (*Z. physiol. Chem.*, 1923, 126, 120-129).—Octa-acetylmaltose reacts with phosphorus pentachloride at  $104-105^\circ$  to form  $\alpha$ -chloro- $\beta$ (?)-trichloroacetylhexa-acetylmaltose, m. p.  $132-133^\circ$ ,  $[\alpha]_D^{25} +80.0^\circ$ , which forms white needles, soluble in benzene, chloroform, ethyl acetate, acetone, or hot alcohol. On hydrolysis with methyl-alcoholic ammonia, maltose is obtained, isolated as maltazone, decomp.  $206^\circ$ . This shows that the maltose grouping is still intact. W. O. K.

**Starch.** F. W. TIEBACKX (*Pharm. Weekblad*, 1923, 60, 338-339).—The phosphorus stated to be always present in starch is

probably contained in an ester group which is removed by gradual hydrolysis on keeping or warming; this explains the increase in conductivity and decrease in viscosity.  
S. I. L.

**Hydrolysis of Starch by the System : Neutral Salts + Amino-acids + Peptone.** HUGO HAEHN (*Biochem. Z.*, 1923, 135, 37—602).—A 1% solution of soluble starch was treated with various quantities of a mixture of *N*/10-solutions of sodium, potassium, and calcium chlorides, with the addition of alanine and eucine and albumose or Witte's peptone. After incubation for 1 day at 37°, the solutions were tested with iodine solution. In many cases, a disappearance of the blue starch iodide colour was observed and particularly with the mixture of salts, amino-acids, and peptone. The liquid reduced Fehling's solution. The author considers the experiments prove the chemical hydrolysis of starch without the intervention of living matter.  
H. K.

**Solvents of some Cellulose Esters.** ERNEST WALTER JOHN MARDLES (*J. Soc. Chem. Ind.*, 1923, 42, 127—136r).—The relative solvent power of single and mixed liquids for some cellulose acetates, nitrates, nitroacetates, and chloroacetates was determined by investigating the temperature at which precipitation occurred on cooling, or where this method failed by finding the amount of a non-solvent required to initiate precipitation. The solubility depends on the specific character of both the liquid and the cellulose ester; it has a high temperature coefficient, and many non-solvents may become solvents when suitably mixed with other solvents, and *vice versa*. In general the solvent power and degree of dispersion of the cellulose esters are highest under conditions which admit of the greatest molecular attraction between the dispersed phase and the dispersing medium.  
G. F. M.

**Hydrolysis of Pectin.** FRANK TUTIN (*Biochem. J.*, 1923, 17, 83).—Theoretical. The author replies to various criticisms of his suggestion that pectin probably is the dimethylisopropenyl ester of pectic acid.  
S. S. Z.

**Lignin.** WALTHER SCHRAUTH (*Z. angew. Chem.*, 1923, 36, 149—152).—Based on observations made by previous workers on the degradation and reduction products and derivatives of lignin, the author develops a theory of the constitution of this substance, which attempts to reconcile the conflicting deductions which have from time to time been made. It is suggested that the fundamental unit of the lignin molecule is formed by the condensation of three molecules of 5-hydroxymethylfurfuraldehyde, which is itself produced by the internal condensation of carbohydrates. The unit so formed will consist of a compact condensed ring system, of which three of the outer rings are furan nuclei, and the other three outer rings and the central ring benzene nuclei. Hence under conditions favouring the fission of the furan rings, benzene derivatives appear as degradation products of lignin, and of the humic acids, etc., which with the efflux of time are developed from the

lignin during coal formation. The theory is further developed to account for the formation of methoxyl groups, ligninsulphonate acids, condensation products from the above fundamental unit and so forth.

G. F. M.

**Transport Experiments with Electrometric Ionisable Derivatives of Hydroxylamine.** WILLIAM A. NOYES and JAMES H. HIBBEN (*J. Amer. Chem. Soc.*, 1923, 45, 355—359).—Qualitative transport experiments have been carried out with aqueous solutions of trimethylamine oxide, hydroxytrimethylammonium salts, methoxytrimethylammonium iodide, ethoxytrimethylammonium bromide, trimethyliodomethylammonium hydroxide, and ethoxytrimethylammonium hydroxide. The solutions in many cases contained 7% of gelatin, and the cathode liquid contained hydrochloric acid. It has been shown that in each case an hydroxy-, a methoxy-, or an ethoxy-group remains with the nitrogen as a part of the kation. The linking of these groups to the nitrogen must therefore be very different from that of the hydroxyl or other atom or group which travels toward the anode during the electrolysis. The resistance of the solutions of trimethylamine oxide hydrate and of ethoxytrimethylammonium hydroxide seems more consistent with the hypothesis that the hydroxyl-ion of these compounds is attached to the nitrogen by a principal valency of such a character that it is only slightly ionised, than with that of the unlocalised polar valency assumed by Lewis and Langmuir (*A.*, 1920, ii, 243).

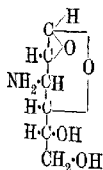
J. F. S.

**Constitution of the Ampholytes, particularly the Amino-acids, and their Dissociation Constants.** NIELS BJERRUM (*Z. physikal. Chem.*, 1923, 104, 147—173).—A discussion of the constitution of ampholytes in which it is shown that the aliphatic amino-acids in an undissociated condition are present almost completely (about 95%) as salt-like double ions  $^+\text{NH}_3\text{RCO}_2^-$ . They are therefore not true amino-acids, but rather ammonium salts. The presence of hydrogen- or hydroxyl-ions in their solutions does not indicate that they are acids, but that hydrolysis of the salt has taken place. The constants  $k_a$  and  $k_b$ , by which the acid and basic character of the amino-acids has hitherto been represented, are not dissociation constants, but rather hydrolysis constants. The real dissociation constants, which give the strength of the acid and base within the neutralised amino-acid molecule, are  $K_A = K_{\text{H}_2\text{O}} : k_b$  and  $K_B = K_{\text{H}_2\text{O}} : k_a$ , where  $K_{\text{H}_2\text{O}}$  is the dissociation constant of water. The values of  $K_A$  and  $K_B$  are such that they are in keeping with the demands of the structural formula. From the nature of the acid and basic groups the values of  $K_A$  and  $K_B$  may be deduced if the influence of the other substituents is taken account of in the usual manner. That the amino-acids contain no free amino-group is confirmed by many chemical reactions, and many physico-chemical properties are in keeping with a salt-like nature rather than with an acid character. This is seen particularly in the fact that they increase the solubility of other

salts, and that they are more soluble in salt solutions than in water. Amongst the aromatic amino-acids, there are also double ions of the form  $^+NH_3 \cdot R \cdot CO_2^-$  and true amino-acids,  $NH_2 \cdot R \cdot CO_2H$ , with free amino- and carboxyl-groups and this true acid may be present in amounts from 10% to 90%. In the case of the aromatic phenols, the double ion form is not present. From the dimensions of the dissociation constants of an ampholyte it is possible to deduce the ratio of the amounts of the two forms present. It is shown theoretically to be probable that for an ampholyte the product  $K_A \cdot K_B$  cannot be smaller than  $4K_{H_2O}$ , that is  $k_a \cdot k_b$  cannot be greater than  $\frac{1}{4}K_{H_2O}$ . From this it follows that the portions of an ampholyte present as anion and kation can never be more than 50%. A number of preliminary experiments confirming the above-mentioned results are recorded.

J. F. S.

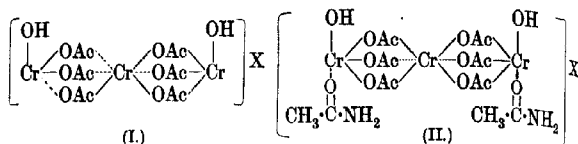
**Epiglucoamine.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1923, 55, 221—227).—When triacetylmethylglucoside- $\beta$ -chlorohydrin (Fischer, Bergmann, and Schotte, A., 1920, i, 420) is heated with concentrated ammonia, methylepiglucoamine is obtained in the form of its acetate, m. p. 214° (corr.) after turning brown at 210°,  $[\alpha]_D^{20} -130^\circ$  in 2.5% hydrochloric acid. The corresponding hydrochloride, long needles, has  $[\alpha]_D^{20} -138^\circ$  in 2.5% hydrochloric acid. Methylepiglucoamine is readily hydrolysed by hydrochloric acid; the isolation of epiglucoamine has not, however, been accomplished owing to the ease with which this compound loses a molecule of water with the formation of *anhydro-epiglucoamine*, which has been isolated in the form of its hydrochloride,  $C_6H_{11}O_4N \cdot HCl$ , m. p. (decomp.) 216° (corr.) after changing colour at 190°,  $[\alpha]_D^{20} -172^\circ$  in 2.5% hydrochloric acid. That epiglucoamine is the first product of hydrolysis has been shown by the preparation from the reaction mixture of its phenylosazone,  $C_{18}H_{22}O_3N_5$ , long, lemon-yellow needles, m. p. 207° (corr.),  $[\alpha]_D^{20} -41^\circ$  (initial) in a solvent composed of four parts of pyridine and six parts of 50% (by volume) methyl alcohol. Anhydroepiglucoamine does not reduce Fehling's solution, but acquires this property on hydrolysis; on the basis of this behaviour, the annexed structure has been assigned to it. That the amino-group is in the  $\gamma$ -position both in this compound and in epiglucoamine follows from the preparation of the osazone of the latter (see above), which excludes the alternative  $\beta$ -position. The space arrangement of this group is, however, quite arbitrary. The configuration of epiglucoamine evidently depends on that of the  $\beta$ - and  $\gamma$ -carbon atoms.



E. S.

**The Addition of Acid Amides to Ferric and Chromic Acetates.** R. WEINLAND and HEINZ HACHENBURG (*Z. anorg. Chem.*, 1923, 126, 285—304).—Compounds formed from ferric or chromic chlorides by the addition of sodium acetate and weakly

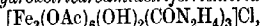
basic acid amides are described and formulae suggested. The general type of the parent compound is shown by (I).



The central chromium atom is the only one exercising its full co-ordination number of 6: the others are co-ordinatively unsaturated and can presumably unite with one, two, or three molecules of an amide to give compounds of which II is typical. The compounds form coloured crystalline powders, brick red in the case of iron, and dark green in the case of chromium. The iron salts are easily soluble in cold water to garnet-red solutions, which are, however, unstable, so that recrystallisation from water is impossible. They are less soluble in alcohol, but decompose in this solvent on long heating. Addition of pyridine to the alcoholic solutions results in the formation of salts with complex kations containing pyridine and four iron atoms, but no amide.

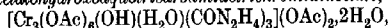
The chromium salts are more stable than those of iron; they are easily soluble in water, giving neutral solutions (in contrast to those of iron, which are weakly acid) which are quite stable, even when boiled. They are less soluble in alcohol than the iron compounds, the solutions being more stable.

*Hexa-acetatodihydroxotricarbamidetriferrichloride,*



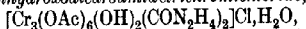
crystallises from an alcoholic solution of hexa-acetatodihydroxotri-ferrichloride and carbamide with  $2\text{H}_2\text{O}$ . The anhydrous salt is obtained by the addition of ether to the mother-liquor. The corresponding *perchlorate* crystallises in small tablets, the *nitrate* forms small, rhombic tablets, and the *chloroferrate* crystallises with  $\text{H}_2\text{O}$  in domed prisms.

*Hexa-acetatodihydroxoquatricarbamidetrichromidiacetate,*



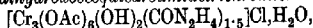
crystallises in green tablets from an aqueous solution of carbamide and the calculated quantity of the diacetate of the hexa-acetatotrichromibase.

*Hexa-acetatodihydroxodicarbamidetrichromichloride,*



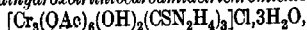
is prepared like the preceding compound, but using the chloride of the base; the corresponding *nitrate* crystallises with  $3\text{H}_2\text{O}$  in right-angled tablets.

*Hexa-acetatodihydroxosquicarbamidetrichromichloride,*



is obtained by the addition of the calculated quantity of carbamide to the preceding chloride.

*Hexa-acetatodihydroxotrihiocarbamidetrichromichloride,*



crystallises in well-defined prisms; the corresponding *nitrate* ( $2\text{H}_2\text{O}$ ) and *perchlorate* ( $2\text{H}_2\text{O}$ ) were prepared.

*Hexa-acetatodihydroxodiacetamidetrichromichloride*,  
 $[\text{Cr}_3(\text{OAc})_6(\text{OH})_2(\text{NH}_2\text{Ac})_2]\text{Cl}$ ,

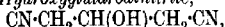
crystallises from an aqueous solution of the hexa-acetatodihydroxotrichromichloride and acetamide in anhydrous crystals and is converted by addition of lithium nitrate into *hexa-acetatodihydroxomonoacetamidetrichrominitrate*. It crystallises with  $2\text{H}_2\text{O}$ ; the corresponding *perchlorate* crystallises with  $\text{H}_2\text{O}$  in prisms. H. H.

**Hydrolysis and Polymerisation of Cyanamide.** H. C. HETHERINGTON and J. M. BRAHAM (*J. Amer. Chem. Soc.*, 1923, 45, 824—829).—The behaviour of cyanamide in both acid and alkaline solution has been studied and the course of the reaction followed by determinations of both cyanamide and carbamide.

By the action of mineral or organic acids, or acid salts, cyanamide is hydrolysed to carbamide, without the formation of dicyanodiamide; the reaction is unimolecular, the velocity of hydrolysis increasing with increasing acid concentration within the limits studied. In alkaline solutions, cyanamide is hydrolysed to carbamide, as well as polymerised to dicyanodiamide, the reaction probably being due to the catalytic influence of the hydroxyl-ion.

Since the presence of acids does not bring about polymerisation, the latter cannot be explained on the equilibrium theory of Werner (T., 1915, 107, 715); the ionic theory suggested by Grube and Kruger (A., 1914, i, 152) is, however, quite satisfactory. W. S. N.

**$\beta$ -Hydroxyglutarodinitrile.** R. LESPIEAU (*Compt. rend.*, 1923, 176, 754—756).— *$\beta$ -Hydroxyglutarodinitrile*,



was obtained as a viscous liquid, b. p.  $202\text{--}203^\circ/11\text{ mm.}$ , by the action of saturated potassium cyanide solution on the chloronitrile,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CN}$ , at a temperature not exceeding  $70^\circ$ . It has  $d_{25}^{25} 1.808$  and  $n_D^{20} 1.4805$ . On saturating with hydrogen bromide, a crystalline mass, m. p.  $230^\circ$ , consisting of the *hydrobromide*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CN}\cdot\text{HBr}$ , is formed, which when decomposed with potassium carbonate yields crystals of  *$\beta$ -bromoglutarodinitrile*, m. p.  $87\text{--}88^\circ$ . G. F. M.

**Hydrocyanic Acid. An Ammono-carbonous Acid, an Ammono-formaldehyde, and a Formic Anammonide.** EDWARD C. FRANKLIN (*J. Physical Chem.*, 1923, 27, 167—186).—A theoretical paper in which an attempt is made to show that hydrogen cyanide possesses simultaneously the properties of an ammonio-carbonous acid, of a formaldehyde of the ammonia system, and of a compound related to ammonia as the unknown formic anhydride is to water. That hydrogen cyanide is an *ammono-carbonous acid*,  $\text{H}\cdot\text{NC}$ , is supported by the following reactions: its formation when carbon is heated in ammonia or a mixture of nitrogen and hydrogen; the action of nitrogen in converting sodium cyanide in the presence of sodium into sodium cyanamide; the formation of sodium cyanamide from sodium cyanide and sodium azide; the formation of sodium dicyanamide by the action of

cyanogen on sodium cyanide; the action of sodamide on carbon, carbon monoxide, and carbon dioxide; the reduction of sodium cyanamide and dicyanimide to sodium cyanide; the oxidation of sodium cyanide to sodium cyanate; the ammonolysis of ethyl carbylamine to ethylamine and hydrocyanic acid; the oxidation of methylcarbylamine to methylcarbimide; and the reduction of hydrogen cyanide to methylamine. That hydrogen cyanide is an *ammono-formaldehyde* is supported by its polymerisation to form compounds of unknown constitution; its condensation to form aldol-like products; its formation of additive compounds with hydrogen sulphites, hydroxylamine, hydrazine, and phenylhydrazine, and by the fact that the relation between hydrogen cyanide and methylamine is the same as that of an aldehyde to an alcohol. That it is *formic anammonide* is shown by the fact that hydrogen cyanide bears an analogous relation to formamide, formamidine, and the formimido-esters, respectively, as acid anhydrides do to acids.

J. F. S.

**Magnesyamine.** I. GIUSEPPE ODDO and EMANUELE CALDERARO (*Gazzetta*, 1923, 53, i, 64–74).—To the compound obtained by treating an organo-magnesium compound, such as magnesium ethyl iodide, in ethereal solution with dry ammonia the authors give, in accordance with the nomenclature proposed by Oddo (A., 1912, i, 721), the name magnesyamine. This product, like Grignard compounds, contains a molecule of ether, its composition being expressed by  $\text{NH}_2\cdot\text{MgX}\cdot\text{Et}_2\text{O}$ . Magnesyamine may be regarded as analogous to sodamide, better termed sodamine, but, unlike the latter, is obtainable easily and with constant properties. In the action of ammonia on magnesium ethyl iodide, the ethane liberated corresponds with only one of the hydrogen atoms of the ammonia:  $\text{MgEtI} + \text{NH}_3 = \text{NH}_2\cdot\text{MgI} + \text{C}_2\text{H}_6$ . Like Grignard compounds, magnesyamine forms with pyridine an *additive* compound,  $\text{NH}_2\cdot\text{MgI}\cdot 2\text{C}_5\text{H}_5\text{N}$ .

Magnesyamine reacts with acid chlorides giving the corresponding amides, the three stages of the reaction with benzoyl chloride being:  $\text{NH}_2\cdot\text{MgI} + \text{Ph}\cdot\text{COCl} = \text{NH}_2\cdot\text{CPhCl}\cdot\text{OMgI}$ , the latter  $+ \text{NH}_2\cdot\text{MgI} = \text{MgClI} + \text{MgIO}\cdot\text{CPh}(\text{NH}_2)_2$ , and the latter  $+ \text{H}_2\text{O} = \text{MgI}\cdot\text{OH} + \text{NH}_3 + \text{NH}_2\text{Bz}$ . With ethyl benzoate, magnesyamine reacts, giving dibenzamide, together with a small proportion of benzamide:  $2\text{Ph}\cdot\text{CO}_2\text{Et} + \text{NH}_2\cdot\text{MgI} = \text{NBz}_2\cdot\text{MgI} + 2\text{EtOH}$  and  $\text{NBz}_2\cdot\text{MgI} + \text{H}_2\text{O} = \text{NHBz}_2 + \text{MgI}\cdot\text{OH}$ ; similarly, the reaction between potassamide and benzoyl chloride yields a mixture of benzamide and dibenzamide. Magnesyamine reacts readily with ethyl phthalate, giving phthalimide, and in ethereal solution unites easily with benzonitrile or nitrobenzene, which are regenerated when the products formed are treated with water.

With benzaldehyde, magnesyamine reacts in two ways, one of the reactions, which yields mainly hydrobenzamide, being analogous to that between aldehydes or ketones and Grignard compounds, and the other to that between sodamide and aromatic aldehydes: (I)  $\text{Ph}\cdot\text{CHO} + \text{NH}_2\cdot\text{MgI} = \text{NH}_2\cdot\text{CHPh}\cdot\text{OMgI}$ ;  $3\text{NH}_2\cdot\text{CHPh}\cdot\text{OMgI} =$

$\text{MgI}\cdot\text{OH} + \text{NH}_3 + \text{MgIO}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OMgI} \rightarrow$   
 $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OH} \rightarrow \text{CHPh}\cdot\text{N}\cdot\text{CHPh}\cdot\text{N}\cdot\text{CHPh}.$   
 (II)  $\text{Ph}\cdot\text{CHO} + \text{NH}_2\cdot\text{MgI} = 2\text{H} + \text{NHBz}\cdot\text{MgI} \rightarrow \text{Ph}\cdot\text{CO}_2\text{NH}_2 +$   
 $\text{MgI}\cdot\text{OH}.$  Magnesylamine and benzophenone yield an additive  
 compound, which gives benzophenone when treated with water.

With acetylacetone, magnesylamine reacts with great readiness, yielding 2:5-dimethylpyrrole:  $\text{CH}_2\text{Ac}\cdot\text{CH}_2\text{Ac} + 2\text{NH}_2\cdot\text{MgI} =$   
 $2[\text{CH}_2\cdot\text{CMe}(\text{NH}_2)\cdot\text{OMgI}] \rightarrow 2[\text{CH}_2\cdot\text{CMe}(\text{NH}_2)\cdot\text{OH}] \rightarrow \begin{matrix} \text{CH}\cdot\text{CMe} \\ \text{CH}\cdot\text{CMe} \end{matrix} > \text{NH}.$

An analogous reaction occurs when acetylacetone is heated in a sealed tube at  $150^\circ$  with a slight excess of alcoholic ammonia (Paal, A., 1885, 1206).

The compound formed from magnesylamine and nitrobenzene gives, with pyridine, a yellow precipitate, consisting of the additive compound,  $\text{MgI}\cdot\text{O}\cdot\text{NPh}(\text{NH}_2)\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{N}.$  T. H. P.

**Action of Acetylene on Zinc Ethyl.** J. F. DURAND (*Compt. rend.*, 1923, 176, 992–993).—Zinc acetylide is formed according to the equation  $\text{C}_2\text{H}_2 + \text{ZnEt}_2 = \text{ZnC}_2 + 2\text{C}_2\text{H}_6$  when acetylene is passed into a solution of zinc ethyl in light petroleum. It is a white substance, decomposed by water with formation of zinc hydroxide, and giving with ammoniacal cuprous chloride a red precipitate of copper acetylide. It is unstable in air, and becomes yellow on warming, owing to the formation of zinc oxide. G. F. M.

**Preparation of Dialkyl Mercury Compounds from the Grignard Reagent. II. Relative Stability of the Carbon-Mercury Linking in Dialkyl Mercury Compounds.** C. S. MARVEL and H. O. CALVARY (*J. Amer. Chem. Soc.*, 1923, 45, 820–823; cf. A., 1922, i, 329).—The reaction between the Grignard reagent and mercury halides has been applied to the production of dialkyl mercury compounds containing secondary and tertiary alkyl groups. The action of heat and of acids indicates that the carbon-mercury linking in  $\text{CR}_2\text{—Hg}$  is less stable than that in  $\text{CHR}_2\text{—Hg}$ , and this in turn less stable than that in  $\text{CH}_2\text{R—Hg}$ . Mercury di-*sec*.-butyl reacts in alcoholic solution with aqueous hydrochloric acid to give *mercuric sec.-butyl chloride*, m. p.  $30.5^\circ$ , and with aqueous hydrobromic acid to give *mercuric sec.-butyl bromide*, m. p.  $39^\circ$ . The Grignard reagent from *sec*.-octyl bromide reacts with mercuric chloride in ethereal solution to give *mercury di-sec.-octyl*, yield 52%, which decomposes when heated, with formation of free mercury; when the above Grignard reagent is treated with mercuric bromide, *mercuric sec.-octyl bromide*, m. p.  $98^\circ$ , is produced. The action of mercuric bromide on the Grignard reagent from *tert*.-butyl bromide leads to *mercury di-tert.-butyl*, b. p.  $78\text{—}82^\circ/5\text{ mm.}$  with decomp.; if an excess of mercuric bromide is used, *mercuric tert.-butyl bromide*, m. p.  $106^\circ$ , decomp., is formed. Similarly, *mercury di-tert.-amyl*, b. p.  $80\text{—}84^\circ/5\text{ mm.}$ , decomp., and *mercuric tert.-amyl bromide*, m. p.  $82^\circ$ , have been obtained.

The indices of refraction of various liquid mercury dialkyl compounds are given.

It is noted that the order of stability towards concentrated

hydrochloric acid is (1) mercury di-*n*-butyl, (2) mercury di-*sec*-butyl, (3) mercury di-*tert*-butyl. Similarly, mercury di-*n*-propyl is more stable than mercury di-*isopropyl*. The same order of stability towards heat is noted.

W. S. N.

**The Problem of Substitution in the Benzene Nucleus and the Thomson-Lewis-Langmuir Theory of Co-valence.** RONALD FRASER and JAMES ERNEST HUMPHRIES (*Chem. News*, 1923, 126, 161—168).—An attempt is made to account for the directive influence of substituents already present in the benzene nucleus in terms of the Thomson-Lewis-Langmuir theory of co-valence. The development of the theory is based on three postulates: (1) the tendency of a disintegrated octet is towards further disruption; and of a nearly completed octet towards completion; (2) the tendency towards octet stability of an atom with nearly completed octet is greater than the tendency to octet instability of an atom with disruption only incipient; (3) the more nearly a group approaches octet stability, the greater the ease of replacement at that point. It is considered that there can be all grades of octet stability between that exhibited in truly polar compounds, where an atom surrounded by a complete octet can exist as a free ion, and that present in typically non-polar compounds. It is shown that an ortho-para-directive substituent, X, has the atom which is linked to the nucleus in a state approaching octet stability; hence the electrons are drawn into X, making the nuclear carbon atom, C<sup>1</sup>, to which it is linked, positive and the ortho- and para-carbon atoms, C<sup>2</sup> and C<sup>4</sup>, negative. A meta-directive substituent, Y, however, such as NO<sub>2</sub>, SO<sub>3</sub>H, etc., has the atom linked to the nucleus in a state of incipient octet disruption; it is therefore positive, C<sup>1</sup> becomes negative, and the meta-carbon atom, C<sup>3</sup>, is also negative, on the principle of induced alternate polarities. Since a negative carbon atom tends to deprive its attached hydrogen atom of its electron, it is evident that a hydrogen atom attached to a negative carbon atom is in a condition favourable for substitution. It follows that a positive substituent such as NO<sub>2</sub>, SO<sub>3</sub>H, etc., is meta-directive, and a negative substituent such as halogen is ortho-para-directive. The terms positive and negative here have the opposite significance to that which they generally carry. Benzene substituents arranged according to the Hollemann series follow a descending order of octet stability. It is shown that a group which favours substitution in the meta-position should favour replacement in the ortho-para-positions, as is well known to be the case. A labile group is one that tends to complete its octet, and is therefore attached to a positive carbon atom. The lability of such a group will be increased by a group such as NO<sub>2</sub> in the ortho- or para-position. The entering group should be of greater octet stability than the one replaced. The theory also explains the loosening effect of ortho-para-directing groups or substituents in the meta-position. On similar lines to the above, the effects of two and three substituents in the benzene ring on the position taken up by an additional substituent are considered. E. H. R.

**The Benzene Formula of Lely.** S. C. J. OLIVIER (*Chem. Weekblad*, 1923, 22, 143—144; J. D. VAN ROON (*ibid.*, 144); H. A. J. SCHOUTISSEN (*ibid.*, 145); H. G. DERX and P. H. HERMANS (*ibid.*, 145—147).—Polemical. Replies to Lely (this vol., i, 99).  
S. I. L.

**Reaction of Nitrosyl Chloride on Toluene.** E. V. LYNN and HELEN L. ARKLEY (*J. Amer. Chem. Soc.*, 1923, 45, [4], 1045—1047; cf. A., 1919, i, 245; 1922, i, 417).—Although nitrosyl chloride is unaffected by benzene, it reacts readily with toluene in the sunlight, giving crystals of benzaldoxime hydrochloride; phenyl-nitrosomethane is presumably the initial product, but is evidently very unstable, since no blue coloration is produced. W. S. N.

**Separation of Xylenes.** H. T. CLARKE and E. R. TAYLOR (*J. Amer. Chem. Soc.*, 1923, 45, 830—833).—The literature dealing with the preparation and separation of the xylenes is contradictory and misleading.

Fractional distillation, selective sulphonation, crystallisation of the sulphonic derivatives, and selective hydrolysis of xylenesulphonic acid all lead to a partial separation of the three xylenes, but none of these processes alone is entirely suitable for the isolation of *o*-xylene and *p*-xylene.

A satisfactory procedure is described in which the above processes are combined [cf. *J.S.C.I.*, 1923, 394A]. W. S. N.

**A New Synthesis of Cumene and *p*-Cymene.** L. BEET (*Compt. rend.*, 1923, 176, 840—842).—Cumene and *p*-cymene were obtained by the action of 1 mol. of magnesium phenyl bromide, and magnesium *p*-tolyl bromide, respectively, on an ethereal solution of 1 mol. of isopropyl sulphate, according to the scheme  $\text{PhMgBr} + \text{SO}_4(\text{CHMe}_2)_2 \rightarrow \text{CHMe}_2\text{Ph} + \text{MgBrSO}_4\cdot\text{CHMe}_2$ . The yield of cumene, b. p. 151—152°/720 mm., amounted to 10%, and approximately the same for *p*-cymene, b. p. 173—175°/720 mm. The substances were each identified by the preparation and isolation of the respective barium sulphonates. G. F. M.

**Primary Tar Oil.** R. WARRINGTON and E. MOEHRLE (*Brennstoff-Chem.*, 1923, 4, 81—84).—Oil from primary tar was freed from phenols and bases, and fractionated under reduced pressure. Unsaturated compounds were removed by dilute sulphuric acid, with which, as they were highly unsaturated, they readily combined. The percentage loss was noted, and the purified residue treated with cold concentrated sulphuric acid to separate aromatic compounds as sulphonic acids, which were afterwards decomposed by steam. The residue consisted of paraffins and naphthenes, which are very difficult to separate, but some success was achieved by the use of fuming nitric acid which attacked the latter. The following compounds were proved to be present in the oil: a homologue of indene,  $\psi$ -cumene, durene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1:6-dimethylnaphthalene. Indications were obtained of the presence of decahydronaphthalene,

dodecahydrodiphenyl, perhydrofluorene, and perhydroacenaphthene. Comparisons are made with coke-oven tar oil. T. S. W.

**Nature of the Hydrocarbons Present in Primary Tar Light Oils.** F. SCHÜTZ (*Brenstoff-Chem.*, 1923, 4, 84).—Hydrocarbons are the chief constituents of primary tar light oil—the following series occurring with very few gaps in the homologues: Paraffins,  $C_nH_{2n+2}$ ; olefines,  $C_nH_{2n}$ ; diolefines,  $C_nH_{2n-2}$ ; cyclic diolefines,  $C_nH_{2n-4}$ ; aromatic hydrocarbons,  $C_nH_{2n-6}$ ; reduced aromatic hydrocarbons (naphthenes). The chief constituents of primary coal tar "benzine," the light oil fraction boiling up to  $150^\circ$ , are aromatic hydrocarbons, then come the olefines in much smaller amounts, whilst only very small quantities of paraffins and other hydrocarbons are present. In researches on "benzines" from other tars (Fischer and Gluud, A., 1919, i, 379), little or no benzene was found, pentane and hexane chiefly being isolated. The cause of the difference may lie in the origin of the coal, or more probably in the method of distillation employed.

T. S. W.

**Occurrence of Ketones and Aldehydes together with Sulphur Compounds in Primary Tar Light Oil.** F. SCHÜTZ (*Brenstoff-Chem.*, 1923, 4, 84; cf. *J. Soc. Chem. Ind.*, 1923, 175A).—The 30–75° fraction of the light oil from primary tar contains about 14% of acetone, corresponding with 0.5 to 1 kg. per ton of coal. Acetaldehyde, paracetaldehyde, acetonitrile, methyl mercaptan, dimethyl sulphide, and carbon disulphide are present in smaller amounts.

T. S. W.

**The Basic Properties of the Nitro-group.** ÉMILE CHERBULIEZ (*Helv. Chim. Acta*, 1923, 6, 281–286).—When an equimolecular mixture of nitrobenzene and sulphuric acid monohydrate is cooled to  $-10^\circ$  to  $-20^\circ$ , after some delay the liquid crystallises in very pale green needles, m. p.  $11^\circ$ , having the composition  $C_6H_5 \cdot NO_2 \cdot H_2SO_4$ . That the crystals are really those of a compound is shown by the fact that crystallisation of the equimolecular mixture cannot be induced by crystals of either nitrobenzene or of sulphuric acid, but is started at once by a crystal of the new compound. By water and by solvents not miscible with sulphuric acid, the compound is split into its constituents, but it can be crystallised by cooling from an ethereal solution. Further evidence that compounds are formed between nitro-derivatives of hydrocarbons and sulphuric acid is afforded by the observation that nitromethane, nitrobenzene, and the three nitrotoluenes when dissolved in sulphuric acid increase its electrical conductivity. This increase in the case of *p*-nitrotoluene, which has the greatest effect, is about half as great as the increase caused by the weakly basic 1:2:4-dinitroaniline. It is therefore considered that mononitro-derivatives of hydrocarbons are very weak bases forming salt-like compounds with strong acids. In the dinitro-derivatives, this basic character has disappeared, for the dinitrobenzenes diminish the conductivity of sulphuric acid. Perchloric acid

in 70% aqueous solution has a powerful solvent action on nitro-compounds, possibly due to the formation of a loose compound between the acid and the nitro-group. E. H. R.

**Preparation of Potassium and Sodium Arylsulphoniodo-amides.** ELWYN ROBERTS (T., 1923, 123, 849—853).

**Preparation of a New Chloroethyl Ester [ $\beta$ -Chloroethyl Toluene-*p*-sulphonate], and the Treatment of Phenols, Alcohols, and Amino-compounds therewith.** BRITISH DYE-STUFFS CORPORATION, LTD., WILLIAM HENRY PERKIN, and GEORGE ROGER CLEMO (Brit. Pat. 193618).— $\beta$ -Chloroethyl toluene-*p*-sulphonate is obtained in good yield as a colourless syrup by boiling toluene-*p*-sulphonyl chloride with ethylene chlorohydrin for three hours. It boils at 210°/21 mm., and condenses readily with phenols, aromatic alcohols, and amines to give ethers, substituted diamines, etc. Thus on heating with phenol in presence of sodium hydroxide  $\beta$ -chloroethyl phenyl ether,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , a pleasant smelling oil, b. p. 217—220°, is obtained as the main product, together with diphenylethylene ether,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$ , in lesser amount. Similar  $\beta$ -chloroethyl ethers are obtained from the cresols and naphthols. The chloroethyl ethers react readily with amines, giving  $\beta$ -phenoxyethyl derivatives of these bases. Thus  $\beta$ -naphthyl- $\beta$ -chloroethyl ether gives with dimethylamine  $\beta$ -naphthyl- $\beta$ -dimethylaminoethyl ether, of which the hydrochloride, m. p. 185°, has a local anæsthetic action. Benzyl alcohol on treatment with  $\beta$ -chloroethyl toluene-*p*-sulphonate and sodium hydroxide gives benzyl  $\beta$ -chloroethyl ether, b. p. 95—110°/16 mm. This substance also reacts readily with amines, for example, from diethylamine benzyl  $\beta$ -diethylaminoethyl ether is obtained.  $\beta$ -Chloroethyl toluene-*p*-sulphonate reacts with amines in presence of sodium carbonate; on heating with aniline, for example, a mixture of diphenylethylenediamine, and diphenylpiperazine is obtained, whilst with methylaniline the main product is diphenyldimethylethylenediamine,  $\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh}$ , and some methyl- $\beta$ -chloroethylaniline, b. p. 124°/10 mm., is obtained.  $\beta$ -Chloroethyl toluene-*p*-sulphonate also reacts with *m*-nitrophenols and with aminophenols, yielding chloroethyl ethers, but the amino-group must previously be protected by acetylation. *o*-Acetamidophenyl  $\beta$ -chloroethyl ether forms long prisms, m. p. 97—98°.

G. F. M.

**New Type of Synthesis. I. Reaction between Halogen-Alkyl Sulphonates and Organomagnesium Halides.** HENRY GILMAN and N. J. BEABER (*J. Amer. Chem. Soc.*, 1923, 45, 839—842).—A preliminary study has been made of the reaction between various organomagnesium halides and halogen-alkyl esters of toluene-*p*-sulphonic acid. In all cases the  $\text{MgX}$  group is replaced by the halogen-alkyl group (cf. Ferns and Lapworth, T., 1912, 101, 273).

The following compounds were obtained with  $\beta$ -chloroethyl-toluene-*p*-sulphonate:  $\beta$ -Chloroethylbenzene, yield 36%, from

bromobenzene;  $\gamma$ -chloropropylbenzene, 59%, from benzyl chloride;  $\beta$ -chloroethylphenylacetylene, 75%, from phenylacetylene, and  $\beta$ -chloroethyl benzoate, 5%, from the benzoate  $\text{PhCO}_2\text{MgBr}$ .  $\gamma$ -Chloropropylbenzene was obtained in 31% yield from bromobenzene and  $\gamma$ -chloropropyl toluene-*p*-sulphonate, b. p. 216–219°/17 mm.,  $d_4^{20}$  1.2674,  $n_D^{20}$  1.5230. W. S. N.

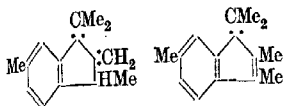
**Sodium Toluene-*p*-sulphochloramide ("Chloramine"), and Its Effect on certain Organic Substances.** N. O. ENGELDT (*Z. physiol. Chem.*, 1923, 126, 1–28).—The action of hypochlorite solutions on various organic substances has already been investigated by the author (cf. A., 1922, 1, 812), and similar experiments have now been carried out with "chloramine." Fats and carbohydrates are found not to react with "chloramine." Amino-acids react very similarly, qualitatively and quantitatively, as with hypochlorite. Hippuric acid, on the other hand, is not affected by the reagent, to which the  $-\text{CO}-\text{NH}-$  linking appears to be resistant. In accordance with this, proteins and peptones are much less affected by the reagent than by hypochlorite. Free ammonia and certain aldehydes also react with it to a much less extent. W. O. K.

**Syntheses in the Indene Series. IV.** A. P. ORÉKHOV [with V. SCHAPIR] (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1820–1826).—2:3-Diphenylindene is synthesised by the dehydration with phosphoric oxide of  $\alpha\beta\gamma$ -triphenylpropane- $\alpha\beta$ -diol, m. p. 159–160°, prepared by the action of magnesium benzyl chloride on benzoin. Dehydration with acetyl chloride gives a 35% yield of the diphenylindene together with a 50% yield of monoacetate of the diol, m. p. 176–177°, which is the sole product of the action of acetic anhydride. R. T.

**Syntheses in the Indene Series. V.** A. P. ORÉKHOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1827–1829).—The method of the synthesis of indenenes from substituted bromopropanes by the elimination of hydrogen bromide, is applied with success to the synthesis of indones. The dibromide of benzylidenedeoxybenzoin,  $\text{COPh-CPhBr-CHPhBr}$ , is heated at 140–145°. A copious evolution of hydrogen bromide takes place and an 89% yield of 2:3-diphenyl-1-indene is obtained. R. T.

**Azulene.** ROLAND E. KREMERS (*J. Amer. Chem. Soc.*, 1923, 45, 717–723).—The isolation of azulene, b. p. 135.6°/1.1 mm., 167–168.4°/11 mm., from oil of milfoil (cf. Sherndal, A., 1915, i, 82, 702) has been slightly modified and the absorption spectrum plotted. The hydrocarbon, b. p. 130–140°/20 mm., produced by complete reduction by means of hydrogen and palladium, has the formula  $\text{C}_{15}\text{H}_{18}$  (cf. Sherndal, *loc. cit.*; also Augspurger, *Science*, 1915, 42, 100), and is dicyclic. Reduction may also be effected, at least partly, by means of sodium amalgam, but not by aluminium amalgam. Azulene forms ill-defined additive products with bromine, nitrogen trioxide, and nitrosyl chloride, and apparently

forms also a sodio-derivative from which the hydrocarbon is regenerated by means of hydroxylic reagents. The oxidation of azulene (for which the annexed formulæ are proposed) by means of alkaline potassium permanganate, leads to carbon dioxide, acetone, acetic acid, and (probably) methylphthalic acid.



W. S. N.

**The Binary Eutectics between Naphthalene, Iodoform, and Iodine.** A. M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1779—1785).—The melting points and the composition of the binary eutectic mixtures of naphthalene, iodoform, and iodine are determined, in order to test the accuracy of a theory put forward by Flavitzki (A., 1906, ii, 152). According to this theory, where  $t_1$ ,  $t_2$ , and  $t_3$  are the melting points of three substances, of molecular weight  $M_1$ ,  $M_2$ , and  $M_3$ ,  $t_{1-2}$ ,  $t_{2-3}$ , and  $t_{3-1}$ , the melting points of the eutectic mixtures obtained from each pair, and  $n_{1-2}M_1 + M_2$ ,  $n_{2-3}M_2 + M_3$ , and  $n_{3-1}M_3 + M_1$  are the compositions of these eutectics, the following expressions are obtainable:  $[n_{1-2}^2 M_1(t_1 - t_{1-2})]/[M_2(t_2 - t_{1-2})] = \alpha$ ,  $[n_{2-3}^2 M_2(t_2 - t_{2-3})]/[M_3(t_3 - t_{2-3})] = \beta$ ,  $[n_{3-1}^2 M_3(t_3 - t_{3-1})]/[M_1(t_1 - t_{3-1})] = \gamma$ .

According to Flavitzki, the product  $\alpha\beta\gamma$  should be equal to unity. The results obtained for the systems naphthalene-iodoform, iodoform-iodine, and iodine-naphthalene are in satisfactory agreement with this hypothesis,  $\alpha\beta\gamma$  being 1.113.

R. T.

**Action of Benzylidenemethylamine on certain Aromatic Nitro-derivatives.** MICHELE GIUA (*Gazzetta*, 1923, 53, i, 53—56).—The author has investigated the action of benzylidenemethylamine on 2 : 3 : 4- and 2 : 4 : 5-trinitrotoluenes, and 1-chloro- and 1-bromo-3 : 4 : 6-trinitrobenzenes. These compounds contain a labile nitro-group, and the last two also a labile halogen atom, which, however, is replaced less readily than the nitro-group. The reaction of the labile nitro-group with benzylidenemethylamine is similar to that with methylamine, and is expressed by the equations:  $\geq C \cdot NO_2 + CHPh \cdot NMe + H_2O \Rightarrow \geq C \cdot NHMe + Ph \cdot CHO + HNO_2$  and  $CHPh \cdot NMe + HNO_2 = Ph \cdot CHO + CH_3O + N_2$ . With the chloro- and bromo-trinitrobenzenes, the halogen atom also is replaced by NHMe if excess of the base is employed.

The hydrolysis of various bases, such as benzalazine, the phenylhydrazones, and benzylideneaniline by nitrohalogen compounds containing only the halogen atom in a labile condition was observed by Ciusa (A., 1906, i, 962), but these bases are not hydrolysed by nitro-compounds containing only a labile nitro-group. No hydrolysis of acetoxime, benzophenonephenylhydrazone, or benzylideneaniline occurs when these bases are heated with 2 : 3 : 4- or 2 : 4 : 5-trinitrotoluene, additive compounds being formed with the last two bases.

The interaction of benzylidenemethylamine and 2 : 3 : 4-trinitrotoluene yields 4 : 6-dinitromethyl-*m*-toluidine (cf. Brady and

Gibson, T., 1921, 119, 98); that of benzylidenemethylamine and 2:4:5-trinitrotoluene, 2:4-dinitromethyl-*m*-toluidine (Brady and Gibson, *loc. cit.*), and that of benzylidenemethylamine and 1-chloro-3:4:6-trinitrobenzene, 4:6-dinitrodimethyl-*m*-phenylenediamine (cf. Blanksma and Meerum Terwogt, A., 1902, i, 715).

5-Bromo-2:4-dinitromethylaniline,  $C_6H_3Br(NO_2)_2 \cdot NHMe$ , prepared from 1-bromo-3:4:6-trinitrobenzene and benzylidene-methylamine, forms yellow crystals, m. p. 149–150°. T. H. P.

**Action of Methyl Sulphate on Diphenylamine and on Diphenylmethylamine.** CHARLES STANLEY GIBSON and DUDLEY CLOETE VINING (T., 1923, 123, 831–837).

**Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. I. Preliminary Investigations.** CHARLES A. KRAUS and GEORGE F. WHITE (J. Amer. Chem. Soc., 1923, 45, 768–778; cf. following abstract).—The action of sodium on solutions of various substances in liquid ammonia has been investigated, without, however, any generalisation being reached.

With the exception of triphenylmethane, which forms a sodio-derivative (cf. Schlenk and Thal, A., 1913, i, 1205), hydrocarbons and ethers are unaffected by sodium in ammonia solution; alcohols and phenols form alkoxides and phenoxides, respectively, with liberation of hydrogen. Aldehyde-ammonia forms a similar sodio-derivative, but the behaviour of benzaldehyde has not been fully investigated. The thiophenols form ammonium salts with liquid ammonia, and these are converted by sodium into the sodium salts with formation of hydrogen and regeneration of ammonia. In a similar manner, acetic acid (ammonium salt) gives sodium acetate and hydrogen. Sodium apparently forms an additive product with acetone, or with acetone and ammonia; this is decomposed by water. Propyl iodide gives rise to propane, *n*-hexane, and *n*-propylamine; *tert*-amyl iodide is converted into *sec*-pentane. Ethylene chloride and sodium apparently react quantitatively in liquid ammonia solution in accordance with the equation:  $C_2H_4Cl_2 + 2Na \rightarrow C_2H_4 + 2NaCl$ . Acetylene dibromide and sodium probably react as follows:  $C_2H_2Br_2 + 2Na \rightleftharpoons C_2H_2 + 2NaBr$ ;  $C_2H_2Br_2 + 4Na \rightarrow 2NaBr + C_2Na_2 + H_2$ ;  $C_2H_2 + 2Na \rightarrow H_2 + C_2Na_2$ . *o*-Chlorotoluene is converted into toluene and *o*-toluidine, *p*-chlorotoluene into toluene and *p*-toluidine; both reactions are probably to be expressed as follows:  $2C_6H_4MeCl + 2Na + NH_3 \rightarrow C_6H_5Me + C_6H_4Me \cdot NH_2 + 2NaCl$ . Similarly, dichlorobenzene gives benzene and *o*-phenylenediamine:  $2C_6H_4Cl_2 + 4Na + 2NH_3 \rightarrow C_6H_6 + C_6H_4(NH_2)_2 + 4NaCl$ . Nitrobenzene is reduced successively to azoxybenzene, azobenzene, hydrazobenzene, and aniline, or their sodio-derivatives.  $\alpha$ -Bromonaphthalene is partly converted into naphthalene, whilst from phenylthiocarbimide aniline and diphenyl (traces) are produced. Sodium benzene-sulphonate gives rise to benzene, traces of diphenyl, and sodium sulphite; phenyl sulphide gives benzene and sodium sulphide.

From the product of the action of ammoniacal sodium on benzyl chloride or benzonitrile, no definite compound has been isolated.

W. S. N.

**Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. II. Action of Sodium on Phenyl Halides in Liquid Ammonia.** GEORGE F. WHITE (*J. Amer. Chem. Soc.*, 1923, 45, 779—784; cf. preceding abstract).—Sodium (1 atom) reacts with a phenyl halide (1 mol.) in liquid ammonia with formation of benzene and secondary and tertiary phenylamines, together with sodium halide and occasional traces of aniline, phenylcarbylamine, and sodium cyanide. The fundamental equations are:  $6\text{PhCl} + 6\text{Na} + \text{NH}_3 = 3\text{C}_6\text{H}_6 + \text{NPh}_3 + 6\text{NaCl}$ ;  $4\text{PhCl} + 4\text{Na} + \text{NH}_3 = 2\text{C}_6\text{H}_6 + \text{NPh}_2 + 4\text{NaCl}$ ; and as side-reactions:  $2\text{PhCl} + 2\text{Na} + \text{NH}_3 = \text{C}_6\text{H}_6 + \text{NH}_2\text{Ph} + 2\text{NaCl}$ . The benzene is a primary product, sodium phenyl not being produced. Benzene distils readily, and chlorobenzene and toluene distil slowly, from liquid ammonia mixtures. Diphenylamine and triphenylamine are partly miscible in the solid state, the limits of miscibility being approximately 13% and 75% of triphenylamine. A liquid phase containing 21% of triphenylamine is in equilibrium with the eutectic mixture at 43.6°. The formation of triphenylamine is favoured by dilution of the reaction mixture with light petroleum. Aniline and diphenylamine form sodio-derivatives in liquid ammonia solution.

W. S. N.

**The Synthesis of Optically Active Asparagines.** O. E. LUTZ (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1881—1887).—Various optically active *N*-substituted asparagines are synthesised by the action of aromatic amines on *l*-bromosuccinic acid. In this way, aniline gives *l*-phenylasparagine, m. p. 147—148°, anisidine gives *l*-anisylasparagine, m. p. 135°, and *m*-toluidine gives *l*-*m*-tolylasparagine, m. p. 160—161°. These substances slowly lose their *l*-rotatory power if kept for some time with mineral acids. R. T.

**$\beta$ -Arylamino-ethanols.** ROGER ADAMS and J. B. SEGUR (*J. Amer. Chem. Soc.*, 1923, 45, 785—790).— $\beta$ -Aminoethanols have been synthesised as follows: (1) the condensation of  $\beta$ -chloroethyl chloroformate with a primary amine in benzene solution, with formation of a  $\beta$ -chloroethyl carbamate; (2) the action of aqueous or alcoholic sodium or potassium hydroxide (1 mol.) on the  $\beta$ -chloroethyl carbamate, to give an oxazolidone; (3) the action of aqueous or alcoholic sodium or potassium hydroxide (4 mols.) on the oxazolidone. The last two reactions may be carried out in a single operation.

The following compounds are described.  $\beta$ -Chloroethyl *o*-tolylcarbamate, white needles, m. p. 45°, b. p. 209—210°/37 mm.  $\beta$ -Chloroethyl *p*-tolylcarbamate, white crystals, m. p. 61°.  $\beta$ -Chloroethyl *o*-chlorophenylcarbamate, white needles, m. p. 56.5—57°.  $\beta$ -Chloroethyl *p*-chlorophenylcarbamate, white needles, m. p. 62—63°.  $\beta$ -Chloroethyl *p*-ethoxyphenylcarbamate, white needles, m. p. 94°. 3-*o*-Tolyl-2-oxazolidone, straw-coloured oil, b. p. 180—185°/3 mm. 3-*p*-Tolyl-2-oxazolidone, white needles, m. p. 91°. 3-*o*-Chloro-

*phenyl-2-oxazolidone*, straw-coloured oil, b. p. 185—188°/3 mm.  
*3-p-Chlorophenyl-2-oxazolidone*, white needles, m. p. 118·5—119°.  
*3-p-Phenethyl-2-oxazolidone*, white crystals, m. p. 96°.  $\beta$ -*Anilinoethyl alcohol*, an oil, b. p. 280—285°/755 mm. or 167—170°/19 mm.  
 $\beta$ -*o-Toluidinoethyl alcohol*, an oil, b. p. 145—150°/3 mm.  $\beta$ -*p-Toluidinoethyl alcohol*, a straw-coloured oil, b. p. 153—155°/4 mm., and white plates, m. p. 42—43°.  $\beta$ -*o-Chloroanilinoethyl alcohol*, a straw-coloured oil, b. p. 148—152°/3 mm.  $\beta$ -*p-Chloroanilinoethyl alcohol*, white needles, m. p. 77—77·5°.  $\beta$ -*p-Phenetidinoethyl alcohol*, white crystals, m. p. 68·5—69°.

It is shown that the physiological properties of 3-p-phenethyl-2-oxazolidone are very similar to those of phenacetin. W. S. N.

**Decomposition of Aryl Formamides. Preparation of Substituted Carbamides.** A. MAILHE (*Compt. rend.*, 1923, 176, 689—691).—The catalytic decomposition of arylformamides, for example, formanilide, by alumina at 400° results mainly in the formation of aniline and carbon monoxide. Dehydration occurs to a relatively small extent with production of benzonitrile according to the scheme  $\text{H}\cdot\text{CO}\cdot\text{NHPh} \rightarrow \text{H}_2\text{O} + \text{PhNC} \rightarrow \text{PhCN}$ . The water produced also reacts to a slight extent with the carbylamine to give aniline and carbon monoxide, and with the formanilide to give aniline and formic acid, which in its turn is resolved into carbon dioxide and hydrogen. Contact with nickel at 340—350° also causes resolution of formanilide into aniline and carbon monoxide, but at 400—410° with rapid passage of the vapours, the aniline interacts with unchanged formanilide to give diphenylcarbamide:  $\text{H}\cdot\text{CO}\cdot\text{NHPh} + \text{PhNH}_2 \rightarrow \text{H}_2 + \text{CO}(\text{NHPh})_2$ , which crystallises in the outlet tubes and in the condensate. The formotoluidides behave in a perfectly analogous manner; *di-o-tolylcarbamide*, m. p. 243°, *di-m-tolylcarbamide*, m. p. 203°, and *di-p-tolylcarbamide*, m. p. 241°, were thus prepared. G. F. M.

**New Method of Preparing Tetra-substituted Carbamides.** A. MAILHE (*Compt. rend.*, 1923, 176, 903—905).—The catalytic decomposition by nickel at 400° (cf. preceding abstract) of formo-o-xylidide, m. p. 97°, gives *di-o-xylidylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$ , m. p. 236°, whilst formo-1-methyl-3-ethylphenyl-6-amide, m. p. 151°, yields *s-dimethylethylphenylcarbamide*, m. p. 215°. The formyl derivatives of secondary aromatic amines react in a precisely analogous manner giving tetra-substituted carbamides together with hydrogen, and carbon monoxide and dioxide, and a certain amount of regenerated amine according to the equations:  $\text{NMePh}\cdot\text{COH} = \text{CO} + \text{NHMePh}$ , and  $\text{NMePh}\cdot\text{COH} + \text{NHMePh} = \text{H}_2 + \text{CO}(\text{NMePh})_2$ . Thus methylformanilide, a yellow viscous liquid, b. p. 286°, gives a mixture of methylaniline and *diphenyldimethylcarbamide*,  $\text{CO}(\text{NMePh})_2$ , b. p. 245—246°. Ethyl-o-toluidine gives a formyl derivative, b. p. 272°, which is similarly catalysed to *di-o-tolyl-diethylcarbamide*, b. p. 258—260°, and 1-methyl-3-ethylphenyl-6-amine gives a formyl derivative, m. p. 141°, which is catalysed to *dimethylethylphenyldiethylcarbamide*,  $\text{CO}(\text{NEt}\cdot\text{C}_6\text{H}_3\text{MeEt})_2$ , a yellow liquid, b. p. 295°. G. F. M.

**The Constituents of Lignite Tars. Lignite Tar Creosote Oils.** R. AVENARIUS (*Z. angew. Chem.*, 1923, 36, 165—168).—

These oils are composed of phenols and small quantities of carboxylic acids, the latter occurring almost exclusively in low-temperature tars. Lignite itself has been shown to contain both phenols and acids (Hoffmann, *Z. angew. Chem.*, 1921, 34, 217; Erdmann, *ibid.*, 309, also *J. Soc. Chem. Ind.*, 1921, 570A). The carboxylic acids, extracted with sodium carbonate, undergo decomposition when distilled at atmospheric pressure and even to some extent on distillation under diminished pressure. They are readily converted into their methyl esters and these submitted to fractional distillation under diminished pressure, although here, as in the case of the free acids, a sharp separation is impossible. Fractions boiling within ranges of  $10^\circ$  were collected separately and analysed. The results show that the acids are monobasic and contain a decreasing percentage of hydrogen with increasing molecular weight. The lower fractions comprised mainly acids of the type  $C_nH_{2n-2}O_2$ , whilst the higher contained also those of the type  $C_nH_{2n-4}O_2$ . The presence of esters of unsaturated acids was shown by the behaviour of the fractions towards potassium permanganate and bromine. Treatment with the latter, followed by distillation, destroyed the esters of the unsaturated acids, leaving unaltered those of the acids of the type  $C_nH_{2n-2}O_2$ . The latter appeared to be saturated naphthenic acids (e.g. the esters  $C_9H_{13}\cdot CO_2Me$  and  $C_9H_{15}\cdot CO_2Me$ , boiling at  $103\text{--}106^\circ/13$  mm. and  $127\text{--}133^\circ/12$  mm., respectively, are found in the mixture of esters after treatment as above).

The crude phenols, containing water, were submitted to repeated fractional distillation under diminished pressure and the individual fractions treated, in absolute ethereal solution, with carbamyl chloride, whereby crystalline carbamic and allophanic esters were obtained. The former were fractionally crystallised from light petroleum or benzene (they are hydrolysed by boiling water), whilst the allophanates, which were insoluble in the above two solvents, were crystallised from dilute methyl alcohol. These esters were identified both by analysis and by comparison with the carbamates and allophanates of a number of homologues of phenol, synthesised specially for the purpose.

By these means phenol itself was found to be absent, whilst the occurrence of *m*-cresol and *p*-xylenol was proved. The aromatic, unlike the aliphatic, carbamic esters decompose in the neighbourhood of their m. p. When distilled, the original phenol and cyanic acid are produced, part of the latter polymerising and remaining in the distillation flask as cyanuric acid. This is a useful method for recovering phenols from their carbamic esters. A similar difference exists between aromatic and aliphatic allophanates. Thiophenols were found in the creosote oil, mainly in the higher fractions. The following esters were synthesised for reference: Phenyl carbamate, colourless needles, m. p.  $143^\circ$ . *o*-Tolyl carbamate, colourless needles, m. p.  $155^\circ$ . *m*-Tolyl carbamate,

colourless, lance-like crystals, m. p. 115—116°. *p*-Tolyl carbamate, colourless needles, m. p. 154°. *m*-4-Xylyl carbamate, colourless needles, m. p. 156°. *p*-Xylyl carbamate, colourless, star-like clusters of needles, m. p. 113—114°. *o*-4-Xylyl carbamate, needles, m. p. 123—133°.  $\psi$ -Cumyl carbamate, colourless needles, m. p. 151—152°. All these esters melt to clear liquids which become cloudy on further heating. *Allophanic* esters: *phenyl*, short, colourless needles, m. p. 178°. *p*-Tolyl, colourless needles, m. p. 199—200°. *m*-4-Xylyl, colourless needles, decomp. at about 220°. *p*-Xylyl, colourless needles, m. p. 203°. *o*-4-Xylyl, needles, m. p. 183°.  $\psi$ -Cumyl, colourless needles, m. p. 213°. W. T. K. B.

**Stereochemistry of Cyclic Alcohols, Aldehydes, and Carboxylic Acids.** A. SKITA (*Annalen*, 1923, 431, 1—30).—Use has been made of the method already described (A., 1922, i, 534) to determine the configurations of the six methylcyclohexanols, the hexahydro-*o*-toluic acids and the hexahydro-*p*-toluic acids, but the configuration of the only known form of hexahydro-*m*-toluic acid remains undecided.

[With H. HÄUBER and R. SCHÖNFELDER].—The reduction of *o*-cresol by means of colloidal palladium and hydrogen in neutral solution gives an 80% yield of 1-methylcyclohexan-2-one, together with traces of *cis*-1-methylcyclohexan-2-ol. Continued reduction under similar conditions of the ketone or of *o*-cresol leads to an 81% yield of *trans*-1-methylcyclohexan-2-ol, which is also produced in 81% yield when the ketone is reduced by means of sodium in moist ethereal solution. The reduction of *o*-cresol or of the ketone by means of palladium-hydrogen in acetic acid solution leads to a 75% yield of the *cis*-alcohol (above), which is converted by means of fuming hydriodic acid into *cis*-2-iodo-1-methylcyclohexane, yield 64%. This iodo-compound reacts with magnesium and carbon dioxide in ethereal solution to give a poor yield of *cis*-1-methylcyclohexane-2-carboxylic acid, which is also formed by the reduction of *o*-toluic acid by means of palladium-hydrogen in acetic acid solution, yield 83%. Incidentally, cyclohexane-carboxylic acid is prepared in 83% yield from benzoic acid by the same method. The *trans*-alcohol (above) yields the *trans*-iodo-derivative, from which *trans*-1-methylcyclohexane-2-carboxylic acid is prepared, in 20% yield. The ethyl ester of the *cis*-acid is reduced by means of sodium and alcohol in 38% yield to *cis*-1-methylcyclohexyl-2-carbinol, which is oxidised by means of chromic acid in acetic acid solution to *cis*-2-aldehydro-1-methylcyclohexane, yield 35%. Similarly, the ethyl ester of the *trans*-acid yields the *trans*-carbinol and the *trans*-aldehyde. The *cis*-acid is quantitatively converted into the *trans*-acid by treatment with gaseous hydrogen chloride.

*trans*-1-Methylcyclohexan-4-ol results from the reduction of *p*-cresol in neutral solution; in acid solution, the *cis*-alcohol is formed. From these, the *trans*-iodo- and the *cis*-iodo-derivatives, respectively, are formed by the action of fuming hydriodic acid; both iodo-compounds lead, however, to the same *trans*-1-methyl

cyclohexane-4-carboxylic acid. This acid is also produced by the action of gaseous hydrogen chloride on the mixture of *cis*-acid and *trans*-acid which is formed by the catalytic reduction of *p*-toluic acid in acid solution. The reduction of the amide of *p*-toluic acid by means of palladium-hydrogen in acid solution gives a 96% yield of the amide of *cis*-1-methylcyclohexane-4-carboxylic acid, which is converted by means of nitrous acid into the *cis*-acid; the latter, being unstable, is esterified before purification. The ethyl ester of the *trans*-acid, from which the *trans*-amide is prepared, and the ethyl ester of the *cis*-acid, both give, on reduction by means of sodium and alcohol, *trans*-1-methylcyclohexyl-4-carbinol in 38% yield; from this the *trans*-aldehyde is obtained on oxidation by means of chromic acid in acetic acid solution; yield 25%.

*m*-Cresol gives *cis*-1-methylcyclohexan-3-ol on reduction in acid solution, *trans*-1-methylcyclohexan-3-ol in neutral solution. Both these alcohols lead, by the action of hydriodic acid, to the same iodo-derivative, which is converted by treatment with magnesium and carbon dioxide in ethereal solution into the only known form (liquid) of 1-methylcyclohexane-3-carboxylic acid; the latter is also produced by the catalytic reduction of *m*-toluic acid in acid solution. The reduction of the ethyl ester of the acid by means of sodium and alcohol leads to 1-methylcyclohexyl-3-carbinol, which gives the corresponding aldehyde on oxidation.

A *heptanaphthenecarboxylic acid* from Balachany petroleum, *n*. p. 190—192°, amide, *m*. p. 126°, has been shown to be different from any of the five known hexahydrotoluic acids.

It is shown that the physical constants of the compounds dealt with conform, with few exceptions, to Auwers's generalisation A., 1920, i, 721).

The following compounds are new. *cis*-1-Methylcyclohexan-2-ol, *n*. p. 169.5—170.5° (corr.), and its phenylurethane, *m*. p. 95°. Phenylurethane of *trans*-1-methylcyclohexan-2-ol, *m*. p. 105°. *cis*-1-Iodo-1-methylcyclohexane, *b*. p. 96°/30 mm. *cis*-1-Methylcyclohexyl-2-carbinol, *b*. p. 188—189°; its benzoate, an oil. *cis*-2-Aldehydo-methylcyclohexane, *b*. p. 70°/24 mm., semicarbazone, *m*. p. 137—38°. *trans*-1-Methylcyclohexyl-2-carbinol, *b*. p. 192—192.5°, benzoate, an oil. *cis*-1-Methylcyclohexan-4-ol, *b*. p. 173.5—173.8°, phenylurethane, *m*. p. 98°. Phenylurethane of *trans*-1-methylcyclohexan-4-ol, *m*. p. 124—125°. *trans*-1-Methylcyclohexyl-4-carbinol, *n*. p. 197.5—198.5°, benzoate, an oil. *trans*-4-Aldehydo-1-methylcyclohexane, *b*. p. 75—76°/24 mm., semicarbazone, *m*. p. 183°. Phenylurethane of *cis*-1-methylcyclohexan-3-ol, *m*. p. 91°. Phenylurethane of *trans*-1-methylcyclohexan-3-ol, *m*. p. 76°. 1-Methylcyclohexyl-3-carbinol, *b*. p. 198—199°, benzoate, an oil. 3-Aldehydo-methylcyclohexane, *b*. p. 95°/35 mm., and its semicarbazone, *m*. p. 75.5°.

W. S. N.

The Fusion Curves of Binary Mixtures of  $\alpha$ -Nitronaphthalene with the three Dihydroxybenzenes and of the Dihydroxybenzenes with Each Other. PIERRE SENDEN (*Bull. Soc. chim. Belg.*, 1923, 32, 97—102).—A study of the fusion curves of binary

mixtures of  $\alpha$ -nitronaphthalene, quinol, resorcinol, and pyrocatechol leads to the conclusion that no compounds are formed between any two of these substances. H. J. E.

**The Methylating and Sulphonating Action of Methyl Sulphate on Phenols in the Absence of Water.** L. J. SIMON and M. FRÉJACQUES (*Compt. rend.*, 1923, 176, 900—902).—The action of methyl sulphate on phenol at 100—120° in the absence of water and alkali gives rise to numerous products owing to the superposition of a sulphonating action on the normal methylating action of this reagent. Both the phenol and the anisole formed from it are in part converted into sulphonic acids, and a proportion of the latter is methylated, so that the reaction mixture contains the free sulphonic acids of both phenol and anisole and their methyl esters, together with methyl hydrogen sulphate and sulphuric acid, and methyl ether is evolved, according to the equations:  $\text{PhOH} + \text{Me}_2\text{SO}_4 = \text{PhOMe} + \text{MeHSO}_4$ ;  $\text{PhOMe} + \text{Me}_2\text{SO}_4 = \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{O}$ ;  $\text{PhOH} + \text{Me}_2\text{SO}_4 = \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{O}$ ;  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{SO}_4 = \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Me} + \text{MeHSO}_4$ ;  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{SO}_4 = \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Me} + \text{MeHSO}_4$ . Treatment of anisole by methyl sulphate in the same way gives the same products but in different proportions, and the formation of phenol sulphonic acid shows that a demethylating action occurs to some extent. A similar series of products was obtained from the cresols. The methyl sulphonates are crystalline substances, which distil at 150—160°/1—2 mm. Methyl phenolsulphonate melts at 95°, methyl anisolesulphonate at 30°, the corresponding derivatives from *o*-cresol at 93° and 58° respectively, and from *p*-cresol at 70° and 70° respectively. The methyl sulphonates are themselves methylating agents, readily giving substituted methylamines with primary amines such as aniline and *o*-toluidine, and methyl ethers with phenols in presence of an alkali. G. F. M.

**The Reactions of Esters with Organomagnesium Derivatives.** V. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1870—1874; cf. A., 1914, i, 954; 1916, i, 259, 260; 1917, i, 136).—Ethyl formate is allowed to react with magnesium phenyl bromide in the presence of a small quantity of iodine. The products of this reaction are benzhydryl ethyl ether and dibenzhydryl ether. The formation of these substances is due to the formation of some benzhydryl iodide, which reacts with the bromomagnesium ethoxide produced in the first part of the reaction giving the mixed ether, or with bromomagnesium benzhydryloxy to give the simple ether. The formation of benzhydryl iodide as an intermediate product of the reaction is proved by the formation of tetraphenylethane in the following reaction. Iodomagnesium benzhydryloxy is prepared from excess of magnesium, benzhydryl, and iodine, ethyl formate is added, and the solution boiled. A number of tarry products are formed, from which tetraphenylethane (formed by the elimination of iodine from two molecules of benzhydryl iodide) is separated. The reaction between magnesium  $\alpha$ -naphthyl bromide and ethyl formate gave a quantity of tarry matter from

which some ethyl di- $\alpha$ -naphthylmethyl ether is isolated. This is formed in the same way as the corresponding diphenyl substance in the previous experiment.

R. T.

\* **The Reactions of Iodomagnesium Alkylloxides with Esters.** II. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1875—1881); cf. A., 1915, i, 975).—Iodomagnesium menthyloxide is formed by the action of menthol on magnesium methyl iodide, and an excess of ethyl formate is added. After boiling for twenty hours, menthyl formate is separated from the reaction mixture. Iodomagnesium triphenylcarbinyl oxide is prepared from triphenylcarbinol and magnesium methyl iodide. To this ethyl formate and a little iodine are added, and the mixture is boiled for forty hours. A variety of products results, from which triphenylcarbinyl peroxide is isolated, produced by the action of atmospheric oxygen on the hexaphenylethane formed by the elimination of iodine from two molecules of triphenylcarbinyl iodide. A larger yield of the peroxide is obtained by repeating the previous reaction in the presence of excess of magnesium, and at the same time some ethyl triphenylcarbinyl ether is formed. Iodomagnesium benzhydryloxide is prepared by the action of benzhydrol on magnesium methyl iodide, and is boiled for thirty hours with ethyl formate. In the reaction products, tetraphenylethane, formed from two molecules of benzhydryl iodide by the elimination of iodine, is found, together with dibenzhydryl ether and benzhydryl ethyl ether, formed by the interaction of iodomagnesium ethoxide with benzhydryl formate. On repeating this reaction, using an excess of magnesium, an increased yield of tetraphenylethane is obtained, proving that benzhydryl iodide is an intermediate product in the formation of the ethers. The same reaction was repeated, using ethyl acetate instead of ethyl formate, and resulted in the production of tetraphenylethane and of a quantity of tarry matter from which no identifiable product was isolated.

R. T.

**$\beta$ -Hydroxyarylethylamines.** O. HINSBERG (U.S. Pat. 1432291).—The following  $\beta$ -hydroxyarylethylamines are prepared by interaction of aminoacetal with phenols in the presence of sulphuric, hydrochloric, or acetic acid: From phenol,  $\beta\beta$ -di-*p*-hydroxyphenylethylamine, m. p. about 95°; from thymol, di-4-hydroxy-3-isopropylphenylethylamine, colourless needles, m. p. 220°. From *m*-aminophenol,  $\beta$ -hydroxy- $\beta$ -2-amino-4-hydroxyphenylethylamine, flakes. From pyrocatechol,  $\beta$ -hydroxy- $\beta$ -di-*o*-hydroxyphenylethylamine, m. p. 190°. From pyrogallol,  $\beta$ -hydroxy- $\beta$ -trihydroxyphenylethylamine, very unstable. From gallic acid,  $\beta$ -hydroxy- $\beta$ -trihydroxycarboxyphenylethylamine, which is not precipitated when ammonia is added to an aqueous solution of the hydrochloride. Methylaminoacetal and pyrocatechol yield  $\beta$ -hydroxy- $\beta$ -di-*o*-hydroxyphenylmethylethylamine and  $\beta\beta$ -di-*o*-hydroxyphenylmethylethylamine, which can be separated by fractional crystallisation of the hydrochlorides, the former (adrenaline) being the non-crystallising portion. *N*-Diisamylaminoacetal and pyrogallol yield  $\beta$ -hydroxy- $\beta$ -trihydroxy-

*phenylethyl-diisoomylamine* which is precipitated in flakes by the addition of ammonia to a solution of the hydrochloride.  $\beta\beta$ -Di-2-hydroxynaphthylethylamine, from aminoacetal and  $\beta$ -naphthol, has m. p. about  $124^{\circ}$ . Interaction of sodium  $\alpha$ -naphthol-8-sulphonate and aminoacetal, followed by addition of hydrochloric acid and washing with water, yields a *product*, m. p. above  $250^{\circ}$ .

CHEMICAL ABSTRACTS.

**Naphthenic Acids Derived from Japanese Petroleum.** YOSHIO TANAKA and SHOICHIRO NAGAI (*J. Amer. Chem. Soc.*, 1923, 45, 754—756; *J. Chem. Ind. Japan*, 1922, 25, 1031—1044).—By acidifying the waste lyes from the Akita petroleum refinery, a crude mixture of petroleum acids is obtained. Neutral impurities are removed by converting the crude acids into the potassium salts and extracting the aqueous-alcoholic solution by means of light petroleum. The acids are reprecipitated by acidification, and alkyl-sulphuric acids removed by distilling the mixture under reduced pressure after the addition of copper oxide. The distillate is again converted into the potassium salts and the aqueous solution extracted by means of light petroleum. The crude acid produced on acidification is fractionally distilled and the fraction b. p.  $170$ — $220^{\circ}/9$  mm. is converted into a mixture of methyl esters. These are then separated by repeated fractional distillation. *Methyl tridecanaphthenate*, b. p.  $124$ — $126^{\circ}/9$  mm. or  $262$ — $263^{\circ}/760$  mm.,  $d_4^{25}$  0.9622,  $n_D^{25}$  1.4663; *methyl tetradecanaphthenate*, b. p.  $135$ — $137^{\circ}/9$  mm. or  $277$ — $278^{\circ}/760$  mm.,  $d_4^{25}$  0.9644,  $n_D^{25}$  1.4686, and *methyl pentadecanaphthenate*, b. p.  $147$ — $149^{\circ}/9$  mm. or  $296$ — $297^{\circ}/760$  mm.,  $d_4^{25}$  0.9659,  $n_D^{25}$  1.4728, are colourless liquids, possessing a fruity odour. The pure naphthenic acids are obtained as colourless, odourless liquids by hydrolysis of the esters by means of 2*N*-alcoholic potassium hydroxide solution. *Tridecanaphthenic acid*, b. p.  $167$ — $169^{\circ}/9$  mm.,  $d_4^{25}$  0.9916,  $n_D^{25}$  1.4784; *tetradecanaphthenic acid*, b. p.  $178$ — $180^{\circ}/9$  mm.,  $d_4^{25}$  0.9930,  $n_D^{25}$  1.4807, and *pentadecanaphthenic acid*, b. p.  $191$ — $192^{\circ}/9$  mm.,  $d_4^{25}$  0.9941,  $n_D^{25}$  1.4848, have no iodine number, and are not discoloured on exposure to the air.

W. S. N.

**Decomposition of Aminobenzoic Acids by Boiling Water.** L. McMASTER and R. L. SHRINER (*J. Amer. Chem. Soc.*, 1923, 45, 751—753).—*o*-Amino- and *p*-amino-benzoic acids, but not *m*-aminobenzoic acid, are decomposed by boiling water into aniline and carbon dioxide; the reaction is unimolecular, the *ortho*-acid decomposing twice as fast as the *para*-acid. Both *o*-aminobenzoic acid and *p*-aminobenzoic acid are slightly volatile in steam, whilst *m*-aminobenzoic acid is not.

W. S. N.

**Catalysis and Steric Hindrance.** G. VAVON and A. HUSON (*Compt. rend.*, 1923, 176, 989—991).—The catalytic hydrogenation by means of platinum black of cinnamic acid derivatives was studied from the point of view of steric hindrance. The method adopted consisted in mixing 1 mol. proportion of the substance to be studied with 1 mol. of pinene, and after the fixation of 1 mol.

of hydrogen the proportion of the cinnamic acid derivative hydrogenised compared with the total amount of the mixed substances hydrogenised was determined by an observation of the change of rotation produced. The results obtained were strictly in accordance with the theory of steric hindrance, as is seen from the following figures which express the percentage which the dihydrocinnamic acid derivative forms of the total substances hydrogenised: *Series 1.* Cinnamic acid 57,  $\beta$ -methylcinnamic acid 26,  $\alpha$ -methylcinnamic acid 22,  $\alpha\beta$ -dimethylcinnamic acid 19. *Series 2.* Methyl cinnamate 63, methyl  $\beta$ -methylcinnamate 45, ethyl  $\alpha$ -methylcinnamate 26. *Series 3.* Ethyl cinnamate 58, ethyl  $\beta$ -methylcinnamate 31, methyl  $\alpha$ -methylcinnamate 22. *Series 4.* Methyl cinnamate 61, ethyl cinnamate 56, isobutylcinnamate 50, cyclohexylcinnamate 40.

G. F. M.

**Ketens. XLIV. Inorganic Substituted Ketens. H. STAUDINGER and H. SCHNEIDER** (*Helv. Chim. Acta*, 1923, 6, 304—315).—It was to be expected that ketens with inorganic substituent groups such as halogen or hydroxyl would be comparatively stable substances, but this proves not to be the case. Halogen atoms decrease the stability and deepen the colour of ketens. Dichloroketen apparently cannot exist, chloroethylketen is very unstable, bromomethylketen is somewhat more stable and can be isolated. Oxygen-substituted ketens are extremely unstable; the existence of phenoxyethylketen and of diphenoxyketen have been established, but they could not be isolated.

*Diphenylacetic-bromoethylmalonic anhydride* decomposes at 88—89°. By distilling this at 15 mm., *bromoethylketen* was obtained as a reddish-brown, very unstable liquid, b. p.  $-40^\circ$  at 0.03 mm. With aniline, it gives *bromoisobutyranilide*, m. p. 97—98°; with alcohol, it gives ethyl  $\alpha$ -bromoisobutyrate. *Ethoxymethylmalonic acid* has m. p. 112°; with diphenylketen, it forms *diphenylacetic-ethoxymethylmalonic anhydride*, m. p. 86°. No trace of ethoxymethylketen could be obtained by heating the anhydride. *Diethoxymalonic acid* has m. p. 159° (decomp.); *diphenylacetic-diethoxymalonic anhydride* melts with slight decomposition at 101—102°; it gave no diethoxyketen when heated. *Ethyl phenoxyethylmalonate*, b. p. 170—180°/12 mm., was obtained by boiling ethyl bromoethylmalonate with sodium phenoxide solution; *phenoxyethylmalonic acid* forms crystals, m. p. 106°; *diphenylacetic-phenoxyethylmalonic anhydride* crystallises in long needles, decomposing at 94°. Phenoxyethylketen could not be obtained directly from this, but its formation was proved by heating the anhydride with benzophenone-aniline, when the  $\beta$ -lactam of  $\beta$ -anilino- $\alpha$ -phenoxy- $\beta\beta$ -diphenyl- $\alpha$ -ethylpropionic acid was obtained, colourless needles, m. p. 164°. No  $\beta$ -lactam could be obtained with benzyldeneaniline, or even with the more reactive *p*-methoxybenzyldeneaniline; these did not react with sufficient rapidity with the fugitive keten.

*Methyl diphenoxymalonnate* was prepared from methyl dibromomalonate and sodium phenoxide in methyl alcohol solution; it has m. p. 86°. *Diphenoxymalonic acid*, m. p. 173°, forms, with

diphenylketen, *diphenylacetic-diphenoxymalonic anhydride*, decomposing at 79°. Diphenoxyketen was not isolated, but its formation was proved by obtaining its aniline derivative, *diphenoxyacetanilide*, which was also prepared from diphenoxyacetic acid; it forms white crystals, m. p. 120°. By heating the above anhydride with benzylideneaniline,  $\beta$ -*anilino- $\alpha\alpha$ -diphenoxy- $\beta$ -phenylpropionic- $\beta$ -lactam*, white crystals, m. p. 165°, was obtained, and with methoxybenzylideneaniline,  $\beta$ -*anilino- $\alpha\alpha$ -diphenoxy- $\beta$ -anisoylpropionic- $\beta$ -lactam*, colourless crystals, m. p. 143°. E. H. R.

**Ketens. XLV. Attempts to Prepare an Alleneketen.** H. STAUDINGER and H. SCHNEIDER (*Helv. Chim. Acta*, 1923, 6, 316—321).—Attempts to prepare a keten containing the allene structure, by heating the mixed anhydride from benzylidenemalonic acid and diphenylketen were unsuccessful; instead of the keten,  $\text{Ph}\cdot\text{CH}\cdot\text{C}\equiv\text{C}\cdot\text{O}$ , only diphenylketen could be obtained. No better result was obtained by heating *benzylidenemalonic-acetic anhydride*, obtained as a yellow syrup from sodium benzylidenemalonate and acetyl bromide. *Benzylidenemalonic anhydride*,  $\text{C}_{10}\text{H}_6\text{O}_3$ , was obtained by the action of oxalyl chloride on silver benzylidenemalonate in benzene. It forms a pale yellow, hygroscopic, amorphous powder, and is apparently highly polymerised. When heated, it decomposes without formation of any benzylideneketen. When silver benzylidenemalonate is distilled under reduced pressure, it decomposes, among the products being cinnamic acid and phenylacetylene. Attempts to apply the mixed malonic anhydride method to the preparation of isopropylideneketen from isopropylidenemalonic acid failed.

Attempts were also made to apply the same method to the preparation of ketens containing the grouping  $-\text{N}\cdot\text{C}\equiv\text{C}\cdot\text{O}$ . Phenylhydrazinomalonic acid,  $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{H})_2$ , failed to react with diphenylketen and when the mixture was heated only a tar was obtained. *Diphenylhydrazinomalonic acid* was prepared by condensing mesoxalic acid with *as*-diphenylhydrazine in aqueous methyl alcohol; it forms fine needles, m. p. 164°. It decomposes in aqueous solution forming carbon dioxide, hydrocyanic acid, and diphenylamine. It does not react in the cold with diphenylketen; in the hot, complete decomposition occurs. No keten could be obtained from isonitrosobenzylmalonic acid by the action of diphenylketen. E. H. R.

**Utilisation of *p*-Dichlorobenzene for Synthesis in the Diphenic Acid Series.** EDWARD B. HUNN (*J. Amer. Chem. Soc.*, 1923, 45, 1024—1030).—*p*-Dichlorobenzene is converted successively into 2:5-dichloronitrobenzene, 4-chloro-2-nitroaniline, 4-chloro-2-nitrobenzonitrile, 4-chloro-2-nitrobenzoic acid, and 4-chloro-2-aminobenzoic acid; the latter is diazotised in dilute aqueous sulphuric acid solution and the diazotised solution gradually added at 20° to an ammoniacal solution of cuprous oxide. The product is 5:5'-*dichlorodiphenic acid*, straw-coloured plates, m. p. 297°; *anhydride*, nearly colourless needles, m. p. 206° (corr.). 2-Amino-4-chlorobenzamide, colourless, oblong plates, m. p. 181.5° (corr.), is

formed by the action of iron and acetic acid on 4-chloro-2-nitrobenzonitrile, in attempting to prepare 4-chloro-2-aminobenzonitrile. The benzoyl derivative of 4-chloroanthranilic acid, colourless needles, m. p. 223.5° (corr.), and the methyl ester, colourless needles, m. p. 68.5°, are also described.

W. S. N.

**The Molecular Configuration of Polynuclear Aromatic Compounds. II. 4:6:4'-Trinitrodiphenic Acid and its Resolution into Optically Active Components.** GEORGE HALLATT CHRISTIE and JAMES KENNER (T., 1923, 123, 779—785).

**Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. IV. The Simulation of Benzenoid Properties by the Five-carbon Intra-annular Nucleus.** CHRISTOPHER KELK INGOLD, ERNEST ARTHUR SEELBY, and JOCELYN FIELD THORPE (T., 1923, 123, 853—874).

**Equilibrium between Benzaldehyde and Benzoin.** ERNEST ANDERSON and RALPH A. JACOBSON (*J. Amer. Chem. Soc.*, 1923, 45, 836—839).—The benzoin condensation is a reversible process; the equilibrium constant between benzaldehyde and benzoin at 79° is very nearly 0.245. The reagents are brought to equilibrium in 95% alcohol in an atmosphere of nitrogen; the benzoin is determined by precipitation by means of water. When benzaldehyde serves as starting material, equilibrium is reached in one hour, but when benzoin is used, 1.5 hours are required. The usual catalyst, sodium cyanide, is utilised. The solvent used in the most satisfactory method for preparing benzoin is 50% alcohol, from which the product is precipitated.

W. S. N.

**Dihydroxyphenones and Derivatives.** B. H. GNAGY (*J. Amer. Chem. Soc.*, 1923, 45, 805—808).—The preparation is described (cf. Goldzweig and Kaiser, A., 1891, 447) of 2:4-dihydroxy-1-propiofenone, which reacts, in acetic acid solution, with bromine to give 3:5-dibromo-2:4-dihydroxy-1-propiofenone, white crystals, m. p. 148°, *phenylhydrazone*, rosettes of small, short, greenish-yellow needles, m. p. 173°, decomp. The action of resorcinol on butyric acid in the presence of zinc chloride leads to the formation of 2:4-dihydroxy-1-butyrophenone, *phenylhydrazone*, m. p. 191—193°, decomp., which reacts with bromine in acetic acid solution to give 3:5-dibromo-2:4-dihydroxy-1-butyrophenone, silky needles, m. p. 113°, *phenylhydrazone*, yellow, hexagonal crystals, m. p. 155°.

W. S. N.

**Ketens. XLII. The Preparation of Ketens from Malonic Anhydrides.** H. STAUDINGER, H. SCHLUBACH, and H. SCHNEIDER (*Helv. Chim. Acta*, 1923, 6, 287—290).—It was shown some years ago (A., 1913, i, 1339) that dialkylketens could be prepared by heating the mixed anhydrides obtained by the action of diphenylketen on dialkylmalonic acid. Attempts to apply this method to the preparation of aldoketens from mono-substituted malonic acids have failed, since mixed anhydrides are not obtained by the

action of diphenylketen on mono-substituted malonic acids. The reaction failed with methyl-, ethyl-, phenyl-, benzyl-, chloro-, bromo-, and ethoxy-malonic acids as well as with malonic acid itself. In every case, only diphenylacetic anhydride was obtained. The probability is that, by the action of diphenylketen on a mono-substituted malonic acid, a ketencarboxylic acid is formed thus:  $\text{RCH}(\text{CO}_2\text{H})_2 + 2\text{Ph}_2\text{C}:\text{CO} \rightarrow \text{RC}(\text{CO}_2\text{H})_2\text{CO} + (\text{Ph}_2\text{CH}\cdot\text{CO})_2\text{O}$ , the ketencarboxylic acid then forming high-molecular polymerisation products.

In the preparation of sparingly volatile ketens such as dibenzylketen by the above method, difficulty is sometimes experienced on account of the decomposition of diphenylacetic anhydride into diphenylacetic acid and diphenylketen, the latter distilling over whilst the free acid combines with the new keten. In such cases, it has been possible to extract the keten from the anhydride with a solvent. Dichloro- and diethoxy-ketens could not be obtained; they probably cannot exist, since by the method employed a keten such as ethylchloroketen, which has only a short life at  $-80^\circ$ , can be isolated. Very unstable ketens can be recognised by combining them with Schiff's bases, with which they form well crystallised  $\beta$ -lactams.

Attempts to obtain mixed anhydrides of malonic acid with acetic, isobutyric, or benzoic acid were unsuccessful. With oxalic acid, a mixed anhydride was obtained which decomposed, giving a mixture of carbon monoxide and dioxide.

Acetylenedicarboxylic acid reacts slowly with diphenylketen; a crystalline mixed anhydride is not formed, but when the mixture is heated a little carbon suboxide is obtained. Acetonedicarboxylic acid does not form a mixed anhydride with diphenylketen, nor could the expected diketocyclobutane be obtained as a decomposition product of the mixture.

E. H. R.

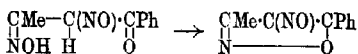
**Ketens. XLIII. Alkyl- and Aryl-substituted Ketoketens.** H. STAUDINGER, H. SCHNEIDER, P. SCHOTZ, and P. M. STROSC (*Helv. Chim. Acta*, 1923, 6, 291—303).—To determine the influence of substituents on the stability and colour of disubstituted ketens, a number of new ketens have been prepared by the decomposition of mixed anhydrides (cf. previous abstract). The stability of the ketens increases considerably with the weight of the alkyl groups in dialkylketens. Whilst at  $25^\circ$  dimethylketen polymerises to the extent of 70% in six hours, diethylketen polymerises only 28% in twenty days and dipropylketen 9% in twenty-eight days. The reactivity towards Schiff's bases decreases with increasing molecular weight, but the colour is unchanged. Dibenzylketen, on the other hand, is less stable than dimethylketen, and in a few hours changes completely into diketotetrabenzylcyclobutane. The influence of the phenyl group is remarkable, for whilst diphenylketen polymerises very slowly, it is more reactive than dimethylketen. In the side chain, the phenyl group diminishes the stability of the keten whilst increasing the reactivity of the ethylene linking. The behaviour of the substituted ketens is paralleled by that of

the corresponding carbimides, of which benzylcarbimide is the most unstable. Diallylketen is a great deal more stable than libenzylketen, polymerising 75% in five days. The instability of the latter cannot therefore be attributed to the  $\beta$ -double bond.

*Diphenylacetic-methylethylmalonic anhydride*,  $C_{20}H_{20}O_4$ , was obtained by adding diphenylketen (2 mols.) to cold methylethylmalonic acid (1 mol.) in ether, and allowing the resulting solution to crystallise. Other mixed anhydrides were prepared similarly. It melts at  $82^\circ$  (decomp.). *Methylethylketen* was obtained by distilling the mixed anhydride under reduced pressure and collecting the distillate at  $-80^\circ$ ; it has b. p.  $-26^\circ$  to  $-28^\circ/12$  mm. *Diphenylacetic-dipropylmalonic anhydride* can be crystallised from a mixture of carbon disulphide and light petroleum; it decomposes at  $84^\circ$ . When distilled under reduced pressure, it gives *dipropylketen*, a yellow liquid with a suffocating odour, b. p.  $30^\circ/11$  mm., the yield being 32% of theory. The yield was determined by converting the keten with aniline into *dipropylacetanilide*, m. p.  $63-104^\circ$ . The polymerisation product of the keten, *diketotetrapropylcyclobutane*, forms colourless crystals, m. p.  $61-62^\circ$ . *Diphenylacetic-dibenzylmalonic anhydride* forms colourless crystals decomposing at  $104^\circ$ . *Dibenzylketen* (cf. preceding abstract) is a bright yellow, mobile liquid, b. p.  $121-122^\circ/0.09$  mm. When the decomposition of the mixed anhydride takes place in presence of benzylidene-aniline, the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenyl- $\alpha$ -dibenzylpropionic acid,  $NPh \langle \begin{smallmatrix} CHPh \\ CO \end{smallmatrix} \rangle C(CH_2Ph)_2$ , is formed, white needles, m. p.  $121^\circ$ . *Diphenylacetic-benzylmethylmalonic anhydride* forms white needles, m. p.  $91^\circ$ . *Benzylmethylketen* is a yellow, mobile fluid with a suffocating odour, b. p.  $45-47^\circ/0.1$  mm. *Diphenylacetic-diallylmalonic anhydride* decomposes at  $95-96^\circ$ . *Diallylketen* is a mobile liquid of unpleasant odour, b. p.  $29-30^\circ/9$  mm., or  $131^\circ/716$  mm., but the latter value is not exact, as some polymerisation occurs. At very low temperatures, it forms a colourless, crystalline mass, m. p.  $-123^\circ$ . *Diallylacetanilide*, prepared to determine the yield of keten (80% theory) has m. p.  $75-76^\circ$ . *Diketotetra-allylcyclobutane* is a colourless liquid, b. p.  $135^\circ/9$  mm. *Ethyl methylallylmalonate*, from ethyl allylmalonate and methyl iodide, has b. p.  $112-115^\circ/17$  mm. *Methylallylmalonic acid* forms white crystals, m. p.  $74-76^\circ$ . *Diphenylacetic-methylallylmalonic anhydride* decomposes at  $69-70^\circ$ . *Methylallylketen* is a suffocating, yellow liquid, polymerising to the extent of 69% in twenty-four hours at  $30^\circ$ . The mixed anhydride from phenylmethylmalonic acid and diphenylketen decomposes in the cold and gives a 75% yield of phenylmethylketen. An attempt to prepare dimethyleneketene from cyclopropanedicarboxylic-diphenylacetic anhydride, white needles, m. p.  $81^\circ$ , was unsuccessful. E. H. R.

**Dioximes. IV. G. PONZIO** (*Gazzetta*, 1923, 53, i, 15-19).—It has been shown previously (A., 1922, i, 1037) that the assumption that the  $\beta$ -oximino-group of  $\alpha$ -benzoylmethylglyoxime may exist in the form  $:CH:NO$  suffices to explain the conversion of this

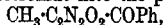
glyoxime into  $\alpha$ -oximino- $\beta$ - $\psi$ -nitroso- $\alpha$ -keto- $\alpha$ -phenylbutane by the action of nitrogen tetroxide. The fact that  $\alpha$ -benzoylmethylglyoxime loses a molecule of water and yields 4-nitroso-5-phenyl-3-methylisooxazole when treated with either acetic anhydride or anhydrous hydrochloric acid may also be explained on the same assumption:



On the other hand, the  $\beta$ - $\gamma$ -dioximino- $\alpha$ -keto- $\alpha$ -phenylbutane structure is supported by the fact that the first of these reagents yields also the diacetyl compound, m. p. 113° (*loc. cit.*), whilst, with both reagents, loss of water occurs likewise in another way,

giving benzoylmethylfurazan,  $\text{O} \begin{array}{c} \text{N:CMe} \\ \text{N:Cbz} \end{array}$ . Both these anhydrides are formed simultaneously when the  $\alpha$ -glyoxime is heated either to the melting point or with water at 80—90°, but under such conditions the formation of the isooxazole compound is manifested only by a transitory bluish-green coloration.

$\beta$ -Benzoylmethylglyoxime (m. p. 193°), which is converted by the action of nitrogen tetroxide into the peroxide,



melts without becoming green, and by acetic anhydride is converted completely into the diacetyl derivative, m. p. 68° (*loc. cit.*), no trace of nitrosoisooxazole being formed. When either heated with acetic anhydride or fused, it is transformed also into benzoylmethylfurazan, whilst the action of anhydrous hydrochloric acid yields a small proportion of 4-nitroso-5-phenyl-3-methylisooxazole in consequence of the preliminary isomerisation of part of the glyoxime into the  $\alpha$ -form.

4-Nitroso-5-phenyl-3-methylisooxazole,  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$  (see above), forms long, flattened, intensely blue needles, m. p. 84°; in the solid state it rapidly undergoes change to a green, and then to an almost colourless, oily substance, and when boiled with dilute sodium hydroxide solution it yields ammonia and benzoic acid.

Benzoylmethylfurazan,  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$  (see above), crystallises in large, white prisms of slight and not unpleasant odour, m. p. 42°, b. p. about 255° (slight decomp.), and is extremely resistant towards even concentrated acids, permanganate in sulphuric acid solution, and chromic acid dissolved in acetic acid, but is decomposed by alkali hydroxide, rapidly when heated, into ammonia and benzoic acid. Its phenylhydrazone,  $\text{C}_{15}\text{H}_{14}\text{ON}_4$ , exists in two modifications: the labile  $\alpha$ -form crystallises in long, golden-yellow needles, m. p. 101°; boiling dilute hydrochloric acid reconverts it into benzoylmethylfurazan, whilst 20% sodium hydroxide solution decomposes it with liberation of ammonia, the bulk of the hydrazone being transformed into the  $\beta$ -form by either of these reagents. The stable  $\beta$ -modification, which is obtained also when the  $\alpha$ -form is heated slightly above its melting point, separates in white or pale yellow laminae, m. p. 214°, and is not sensibly altered when boiled with 20% sodium hydroxide or hydrochloric acid solution. The

*p*-nitrophenylhydrazone,  $C_{16}H_{13}O_3N_3$ , forms flattened, yellow needles, m. p. 178–182°, reddens superficially in the light, and yields a deep violet solution when suspended in sodium hydroxide solution and treated with a little alcohol. The *dinitrophenylhydrazone*,  $C_{18}H_{13}O_5N_5$ , obtained by the action of nitric acid (d 1.2) on either the  $\alpha$ - or  $\beta$ -phenylhydrazone or the *p*-nitrophenylhydrazone, forms orange-yellow laminae, m. p. 218°, with previous softening and reddening; when suspended in 20% sodium hydroxide solution and treated with a little alcohol, it yields a deep violet solution, which is decolorised on dilution with water. T. H. P.

**Dioximes.** V. G. PONZIO and A. PICETTO (*Gazzetta*, 1923, 53, i, 20–24).—Of the two possible dioximes of triketohydrindene, only the 1:3-isomeride, obtained by the action of nitrous acid on  $\beta$ -hydrindone (Heusler and Schieffer, A., 1899, i, 365) is known. The 1:2-dioxime, being analogous structurally to benzoylmethylglyoxime (A., 1922, i, 1037), should be capable of existing in two modifications. The authors find that this 1:2-form may be readily obtained by adding sodium acetate and the theoretical quantity of hydroxylamine hydrochloride to a suspension of 2-oximino-1:3-diketohydrindene in hot alcohol and maintaining the mixture for some time at 60–70°. It exists, however, in only one form, which is neither dehydrogenated nor transformed into the corresponding oximino- $\psi$ -nitroketone-compound by the action of nitrogen tetroxide. It gradually decomposes with evolution of nitrous fumes and, like its phenylhydrazone, crystallises with a molecule of alcohol. Thus, it exhibits certain properties of nitroso-derivatives, but it may be acetylated and benzoyleated and in aqueous solution reacts with metallic nickel.

1:3-Diketohydrindene, for which improved conditions of preparation are given (cf. Wislicenus and Kötze, A., 1889, 1067), forms crystals of the tetragonal system [ZAMBONINI:  $a:c=1:0.984812$ ]; modified conditions are also given for making 2-oximino-1:3-diketohydrindene, which does not form a nickel salt, but when treated in aqueous-alcoholic solution with cobaltous acetate yields a cobaltic salt,  $(C_6H_4(C_2O_2(CNO)_3)_3Co$ , as a micro-crystalline, brownish-yellow powder, m. p. above 300° (decomp.). Thus, 2-oximino-1:3-diketohydrindene acts towards cobaltous salts like  $\alpha$ -benzilmonoxime, whereas other  $\alpha$ -oximinoketones yield cobaltous compounds.

*Triketohydrindene 1:2-dioxime*,  $\begin{array}{c} CO-C:NOH \\ | \\ C_6H_4-C:NOH \end{array}$ , crystallises in white or pale straw-coloured prisms, m. p. 168° (decomp.), containing  $1H_2O$ , which is lost slowly at the ordinary temperature. It dissolves in solutions of alkali hydroxide or ammonia, giving reddish-yellow solutions from which it is precipitated unchanged by the action of carbon dioxide or a dilute mineral acid. With hydroxylamine hydrochloride and sodium acetate, it yields the corresponding trioxime (cf. Wislicenus and Kötze, *loc. cit.*). The nickel compound,  $(C_6H_5O_2N_2)_2Ni$ , forms microscopic, pale yellowish-brown crystals, turning brown at 180°, m. p. above 300°. The

*diacetyl* derivative,  $C_{16}H_{16}O_5N_2$ , is somewhat unstable and forms pale straw-yellow needles, m. p.  $155^\circ$  (decomp.). The *dibenzoyl* derivative,  $C_{22}H_{14}O_5N_2$ , forms microscopic needles, m. p.  $174^\circ$  (decomp.). The *phenylhydrazone*,  $C_{15}H_{12}O_2N_4$ , EtOH, crystallises in orange-red needles, m. p.  $189-190^\circ$  (decomp.). T. H. P.

**Dioximes. VI.** G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, 53, i, 25-35).—The authors have investigated the two modifications of phenylglyoxime, m. p.  $168^\circ$  and  $180^\circ$ , regarded by Russanov (A., 1892, 321) as being the *amphi-* and *anti-*compounds, respectively, and have also obtained a second modification of aminophenylglyoxime. With such isomeric glyoximes, the prefix  $\alpha$  is given to those which readily undergo isomerisation into the other or  $\beta$ -forms, the latter alone being able to form with nickel, copper, or cobalt complex salts derived from two molecules of the glyoxime by replacement of two oximino hydrogen atoms, one from each molecule, by an atom of the bivalent metal. As might be foreseen from the results obtained with the benzoylmethylglyoximes (A., 1922, i, 1037), the two forms of phenylglyoxime behave differently towards nitrogen tetroxide, the  $\alpha$ -form losing two atoms of hydrogen and giving the compound regarded by Scholl (A., 1891, 315) as the peroxide,  $\begin{smallmatrix} O:N\cdot CH \\ | \\ O:N\cdot CPh \end{smallmatrix}$ , and by Wieland

and Semper (A., 1908, i, 108) as phenylfuroxan; the  $\beta$ -form, on the other hand, loses three atoms of hydrogen, one of which is replaced by a nitro-group, the resultant product being phenylnitro-glyoxime peroxide. These results confirm the view that the isomerism of the two phenylglyoximes does not depend on the relative positions of the hydroxyl groups in space.

The conclusion is drawn that  $\beta$ -phenylglyoxime and  $\beta$ -benzoylmethylglyoxime, which yield complex nickel salts, are true dioximes, as they behave towards nitrogen tetroxide as if they contain two similar oximino-groups, the resulting peroxides being unaffected by ammonia.  $\alpha$ -Phenylglyoxime, acetylmethylglyoxime, and  $\alpha$ -benzoylmethylglyoxime, which do not form complex nickel salts, react with nitrogen tetroxide, giving rise, respectively, to the compound  $C_6H_5\cdot C_2H_4O_2N_2$ , which with ammonia yields aminophenylglyoxime, to  $\alpha$ -oximino- $\beta$ - $\psi$ -nitrole- $\gamma$ -ketopentane, and to  $\gamma$ -oximino- $\beta$ - $\psi$ -nitrole- $\alpha$ -keto- $\alpha$ -phenylbutane (A., 1922, i, 627, 1037), which with ammonia yields aminomethylglyoxime. Hence the oximino-group of  $\alpha$ -phenylglyoxime, which is united to the carbon atom carrying the hydrogen atom and originates by the action of nitrous acid on acetophenone, may, like the  $\beta$ -oximino-group of acetylmethyl- or benzoylmethylglyoxime, resulting from the action of nitrous acid on acetyl- or benzoyl-acetone, assume a structure different from that of the oximino-group introduced into isonitrosoacetophenone, isonitrosoacetylacetone, or isonitrosobenzoylacetone by means of hydroxylamine.

The author's results show that Wieland and Semper (*loc. cit.*) are in error in assuming that the various modifications of one and the same dioxime give the same peroxide, even if, as follows from

the work of Korev (A., 1886, 363) and of Auwers and Meyer (A., 1889, 403, 713),  $\alpha$ -,  $\beta$ -, and  $\gamma$ -benzildioximes give the same peroxide when dehydrogenated by means of potassium ferricyanide.

Addition of aqueous nickel acetate to an aqueous alcoholic solution of  $\alpha$ -phenylglyoxime yields the amorphous, brownish-yellow nickel compound, probably  $C_8H_6O_2N_2Ni$ . With nitrogen tetroxide, the  $\alpha$ -glyoxime gives the compound  $C_8H_6O_2N_2$ , m. p.  $108^\circ$ , which is perfectly stable in a stoppered bottle in the dark (cf. Wieland and Semper, *loc. cit.*).

In aqueous solution,  $\beta$ -phenylglyoxime acts on compact nickel, copper, or cobalt, slowly in the cold but rapidly at about  $100^\circ$ , this behaviour being characteristic of the glyoximes which Tschugaev terms *syn*-forms. The nickel salt,  $(C_8H_6O_2N_2)_2Ni$ , crystallises in dark red needles, m. p.  $267^\circ$  (browning); the copper salt,  $(C_8H_6O_2N_2)_2Cu$ , forms a coffee-coloured powder with green reflection, m. p.  $181^\circ$  (decomp.), and the cobalt salt, a coffee-coloured powder with red reflection. Russanov's statement that  $\beta$ -phenylglyoxime is transformed instantaneously into the  $\alpha$ -form by all neutral solvents with the exception of absolute ether (*loc. cit.*) is erroneous. Nitrophenylglyoxime peroxide, obtained by the action of nitrogen tetroxide on  $\beta$ -phenylglyoxime in anhydrous ethereal solution, has the properties given by Wieland (A., 1903, i, 769), who found this compound among the products of the action of nitrous fumes on cinnamaldehyde.

*Chlorophenylglyoxime*,  $NOH:CPh\cdot CCl:NOH$ , prepared either by the action of hydroxylamine on chloro-oximinoacetophenone or by the action of chlorine on  $\alpha$ - or  $\beta$ -phenylglyoxime, exists in only one modification, and crystallises in slender, white needles, m. p.  $189-190^\circ$  (decomp.). Its nickel salt,  $(C_8H_6O_2N_2Cl)_2Ni$ , forms slender, reddish-brown needles, m. p.  $167^\circ$  (decomp.), and its diacetyl derivative,  $C_{12}H_{11}O_2N_2Cl$ , slender, white needles, m. p.  $82^\circ$ .

$\beta$ -Aminophenylglyoxime,  $NOH:CPh\cdot C(NH_2):NOH$ , obtained by boiling its  $\alpha$ -isomeride with dilute acetic acid, and isolated as nickel salt, forms lustrous, white laminae, m. p., with rapid heating,  $195^\circ$  (sublim. and decomp.), and yields an intense brown coloration with ferric chloride. Its nickel salt,  $(C_8H_6O_2N_3)_2Ni$ , forms lustrous, orange-red laminae, m. p.  $265-285^\circ$  (decomp.), and the copper salt,  $(C_8H_6O_2N_3)_2Cu$ , lustrous, bronze-coloured laminae with metallic lustre, m. p., with rapid heating,  $232^\circ$  (decomp.). T. H. P.

**The Transformation of Campholic Acid into Camphor.** H. RUPE and A. SULGER (*Helv. Chim. Acta*, 1923, 6, 259-263).—The benzylidenecampholic acid of Rupe and Blechschmidt,  $CO_2H\cdot C_8H_{14}\cdot CH:CHPh$  (A., 1918, i, 222), reacts with thionyl chloride to form an acid chloride, which, however, when it is distilled under reduced pressure changes with evolution of hydrogen chloride into benzylidenecamphor. The same transformation occurs spontaneously in the course of a few days when a solution of the acid chloride in thionyl chloride is kept. The chloride of benzylcampholic acid, however, is quite stable. The reaction in the case of benzylidenecamphoryl chloride probably takes place through

the intermediate formation of the compound  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CHClPh} \\ \text{CO} \end{smallmatrix}$ , which loses hydrogen chloride forming benzylidenecamphor. In the case of benzylcampholyl chloride, this reaction is, of course, impossible. The influence of ring-closure on optical rotatory power is here very marked, the value for benzylidenecampholic acid being  $[\alpha]_D^{20} + 12.60^\circ$ , and for benzylidenecamphor,  $[\alpha]_D^{20} + 426.55^\circ$ . Camphor derivatives also show a higher rotation dispersion than those of campholic acid. The supposed ethyl ester of benzylidenecampholic acid obtained by Rupe and Blechschmidt from the chloride (*loc. cit.*) is not the ester, but benzylidenecamphor.

E. H. R.

**Derivatives of Buchu-camphor.** YASUHIKO ASAHINA and SATORU KWADA (*J. Pharm. Soc. Japan*, 1923, 1—9; cf. Asahina and Mituhori, A., 1922, i, 667).—The formation of buchu-camphor from menthone by the action of ferric chloride was again studied; but the yield could not be increased beyond 24%. The m. p.,  $113^\circ$ , for the phenylurethane is confirmed (Semmler and Mackenzie, A., 1906, i, 373, gave  $41^\circ$ ). By boiling an alcoholic solution of hydroxylamine hydrochloride, sodium carbonate, and buchu-camphor on a water-bath for five hours under reflux, the monoxime, plates, was obtained, m. p.  $123^\circ$  (Semmler and Mackenzie, *loc. cit.*, give m. p.  $125^\circ$ , Kondakov, A., 1901, i, 334, gives  $156^\circ$ ); its alcoholic solution gave a green coloration with ferric chloride. When the boiling is continued for ten hours, the resulting oxime has m. p.  $154\text{--}157^\circ$ , and the analytical figures suggest that a dioxime is formed. When an alcoholic solution of buchu-camphor, hydroxylamine hydrochloride, and sodium acetate is heated at  $100^\circ$  in a sealed tube for ten hours, the true dioxime, colourless, short prisms, m. p.  $192^\circ$ , is formed; it gives a brownish-red coloration with ferric chloride. When oxidised with potassium permanganate in acetone solution, buchu-camphor is known to yield  $\gamma$ -acetyl- $\alpha$ -isopropylbutyric acid, but when the oxidation is conducted in 5% potassium hydroxide solution at about  $5^\circ$ , a diketonic acid,  $\text{COMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHPr}^2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , large, square plates, m. p.  $135^\circ$ , is produced, which, when distilled at  $190\text{--}195^\circ/11\text{ mm.}$ , or when heated with concentrated hydrochloric acid, is easily changed into the closed ketonic acid,  $\text{CH}_2 \begin{smallmatrix} \text{CO} \text{---} \text{CH} \\ \text{CH}_2 \cdot \text{CHPr}^2 \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , white plates, m. p.  $104^\circ$ . The semicarbazone, white crystals, m. p.  $223^\circ$ ; phenylhydrazone, slender, light yellow prisms, m. p.  $220\text{--}221^\circ$ ; and oxime, white granules, m. p.  $185\text{--}186^\circ$ , of the diketonic acid are identical with those obtained from the closed ketonic acid.

K. K.

**Effect of Fuller's Earth on Pinene and other Terpenes.** CHARLES S. VENABLE (*J. Amer. Chem. Soc.*, 1923, 45, 728—738).—The action of fuller's earth on  $\alpha$ -pinene and other terpenes, with and without diluents, at  $-20^\circ$ ,  $-5^\circ$ ,  $25^\circ$ , and  $153^\circ$  has been investigated.

In contrast to the conclusions of Gurvich (A., 1915, i, 933), the

reaction evidently proceeds as follows: (1) Intramolecular rearrangement to dipentene and terpinene. No camphene is formed. (2) Polymerisation to dipinene and various unidentified polyterpenes. (3) Slow decomposition of the polyterpenes at high temperatures to give paraffin hydrocarbons and *p*-cymene, but not monoterpenes. With increasing temperature of reaction, the proportion of dipinene and polyterpenes to terpenes increases.

Nopinene, dipentene,  $\alpha$ -limonene, terpinene, camphene, sabinene, terpineol, borneol, and cineol undergo similar reactions. *p*-Cymene is quite unaffected by treatment with fuller's earth.

The maximum activity of the fuller's earth is attained when it contains 5–8% of combined moisture (burning temperature about 400°). Oxygenated diluents exert a strong inhibiting action.

Iron gel, silica gel, or activated charcoal do not promote this reaction.

W. S. N.

**Pinenes.** H. PARISELLE (*Ann. Chim.*, 1923, [ix], 19, 119–135).—Previous work on  $\alpha$ - and  $\beta$ -pinenes is again described (cf. A., 1921, i, 575). The preparation of nitrosochlorides of pinene resulted in confirmation of Wallach's observations on the relation of yield to rotatory power, but it is pointed out that the presence of less active  $\beta$ -pinene may lead to inconsistent results. The nitrosochloride formed is always inactive, and the author suggests that  $\alpha$ -pinene consists of a mixture of active and inactive isomerides which are not capable of separation, the latter form yielding the derivative and being itself formed from the active variety. The action of dry hydrogen chloride on  $\beta$ -pinene yields isobornyl chloride, on  $\alpha$ -pinene (from Aleppo turpentine), a crystalline hydrochloride of m. p. 124–128° and  $[\alpha] +35.9^\circ$ , whilst from  $\alpha$ -pinene extracted from Bordeaux turpentine the corresponding product has m. p. 120–126° and  $[\alpha] -32.5^\circ$ . A method of calculating the optical activity of  $\alpha$ -pinene based on the optical purity of  $\beta$ -pinene is given.

H. J. E.

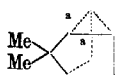
**The Wagner Rearrangement. II. The Formation of Santene.** L. RUTICKA and FR. LIEBL (*Helv. Chim. Acta*, 1923, 6, 267–281; cf. A., 1918, i, 398).—The expectation that by removal of water from  $\alpha$ -fenchocamphorol santene would be formed has been verified. By the action of phosphorus pentachloride on fenchyl alcohol in low-boiling light petroleum,  $\alpha$ -fenchone was obtained having  $[\alpha]_D -38^\circ$  instead of  $-32^\circ$ , as found by Wallach; its other constants were, b. p. 153–154°/720 mm.;  $n_D^{25} 1.4750$ ,  $d_4^{25} 0.870$ . It was oxidised with ozone to  $\alpha$ -fenchocamphorone, of which the semicarbazone gave two fractions from alcohol, a less soluble one having m. p. 217–218°,  $[\alpha]_D -171.5^\circ$ , and the more soluble one m. p. 210–211°,  $[\alpha]_D -141^\circ$ . The  $\alpha$ -fenchocamphorone regenerated from the total semicarbazone had, after sublimation, m. p. 107°. Thionyl chloride with fenchyl alcohol gives *fenchyl sulphite*,  $(C_{10}H_{17}O)_2SO$ , colourless crystals, m. p. 72°. The  $\alpha$ -fenchocamphorone was reduced with sodium and water to  $\alpha$ -fenchocamphorol, and the latter heated with potassium hydrogen sulphate at 190° in a stream of carbon dioxide, when santene distilled over, b. p.

140–142°,  $[\alpha]_D^{20}$  0,  $n_D^{20}$  1.4657,  $d_4^{20}$  0.8720. It was identified by oxidation with ozone to 1:3-diacetylcyclopentane. A mixture of  $\alpha$ - and  $\beta$ -fenchene was prepared by heating fenchyl alcohol with sodium hydrogen sulphate, and from this by the above method a mixed  $\alpha$ - and  $\beta$ -fenchocamphorol was obtained. When this was heated with potassium hydrogen sulphate as above, santene was obtained having practically the same constants as that from  $\alpha$ -fenchocamphorol. It is concluded that both  $\alpha$ - and  $\beta$ -fenchene give the same santene. From santanol, by heating with potassium hydrogen sulphate, santene was also obtained.

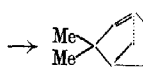
The authors' theory of the formation of an intermediate tricyclic in the course of the Wagner rearrangement (*loc. cit.*) has been rejected by Lipp (A., 1920, i, 491) and by Meerwein and Emster (A., 1920, i, 855), who have prepared the tricyclic and found it to be quite stable under the conditions of the borneol-camphene transformation. The alternative hypotheses suggested by these authors fail, however, to account for the formation of santene, whilst the tricyclic hypothesis offers a clear picture of the mechanism of the reaction. The simplest case is the formation of santene from santanol, when the intermediate tricyclic is represented by I. In the formation of santene from  $\alpha$ -fenchocamphorol,  $\beta$ -fenchocamphorol, and camphenilol, each of these compounds by loss of water can form the same tricyclic, represented by the space-formula II. By rupture of one of the bonds,  $a$ , a double-bond is formed attached to one of the bridge carbon atoms,



(I)



(II.) Tricyclicene.



(III.) Unstable.



(IV.) Santene.

an unstable configuration (III) which can only be stabilised by the wandering of one of the methyl groups, giving santene (IV). It has been urged as an objection to the tricyclic hypothesis that, since the tricyclic is symmetrical, it cannot give rise to an optically active product. This objection, however, can scarcely be maintained, since in the case of the transformation of optically active linalool into active terpineol, in the course of which the active centre is changed from one carbon atom to another, on any hypothesis, there must be a symmetrical intermediate stage. It must be supposed that, in the Wagner rearrangement, formation of the tricyclic and its isomerisation take place simultaneously, and that considerations which apply to the stable tricyclic do not apply to it in the nascent state.

E. H. R.

**$\beta$ -Amyrin from Manila Elemi Resin.** ALEX. ROLLETT (*Monatsh.*, 1923, 43, 413–417).—Alcoholic potassium hydroxide converts dibromo- $\beta$ -amyrin benzoate (A., 1921, i, 39; 1922, i, 667) into an impure potassium derivative, from which, on acidification, only a gelatinous substance is obtained. Bromination of  $\beta$ -amyrin in glacial acetic acid solution gives a mixture of (a) bromo- $\beta$ -amyrin

acetate, m. p. 235—236° (solution in concentrated sulphuric acid yellow, with green fluorescence), and (b)  *dibromo-β-amyrin*, m. p. 210—216° (decomp.). By oxidising β-amyrin with chromic acid, Vesterberg (A., 1892, 290) obtained β-amyrone (oxime, m. p. 262—263°). The latter substance, now called β-amyranone (oxime, m. p. 265—267°), melts at 177—179°. Potassium permanganate affords no isolable oxidation product with β-amyranone. The latter, on heating with benzoyl chloride, yields β-amyrenol benzoate, which melts at 181—182°, gives a yellow solution in concentrated sulphuric acid, and is converted by hot alcoholic potassium hydroxide into β-amyranone.

E. E. T.

**Constituents of Derris-root.** I. TATSUO KABIYONE and KENJIRO ATSUMI (*J. Pharm. Soc. Japan*, 1923, 10—17).—Greshoff (A., 1891, 335) and van Sillevoldt (A., 1900, i, 109) isolated an amorphous poisonous constituent, derrid, from the root of *Derris elliptica*, Benth., and Wray (*Pharm. J.*, 1892, 1152) obtained the constituent tubain. Ishikawa (A., 1918, i, 94) isolated tubotoxin,  $C_{18}H_{18}O_8$ , white crystals, m. p. 163.5°, from the root. The authors confirm Ishikawa's results. The poisonous constituent was proved to have one carbonyl group by the formation of a *phenylhydrazone*, light yellow needles, m. p. 255°, and an *oxime*, colourless needles, m. p. 245°. When heated with sodium acetate and acetic anhydride, tubotoxin gives a *diacetyl* derivative, the saponification value (84.3—116.9) of which is, however, lower than the calculated value (281.8). Estimation of methoxyl by Zeisel's or by Herzig's methods indicated the presence of 1.5-methoxyl groups in tubotoxin. Benzoyl chloride or phthalic anhydride have no action on it. Tubotoxin is probably identical with retelon obtained by Nagai (*J. Tokyo Chem. Soc.*, 1902, 23, 744) from *Millettia taiwaniana*, Hayata, produced in Formosa.

K. K.

**Bixin.** J. HERZIG and F. FALTIS [and, in part, BERTHA PITTMER, FRIEDRICH KLEIN, and GEORG WATZINGER] (*Annalen*, 1923, 431, 40—70; cf. A., 1917, i, 577).—Previous work on this subject, in particular the researches of Hasselt (A., 1911, i, 550; 1916, i, 495), and the facts described below, are discussed on the basis of the formula  $CO_2H \cdot C_{23}H_{26} \cdot CO_2Me$  for bixin, where  $C_{23}H_{26}$  is an unsaturated residue to which the carboxyl and carbomethoxyl groups are unsymmetrically attached.

Bixin, which cannot be esterified by means of alcoholic hydrogen chloride, absorbs eighteen atoms of hydrogen in glacial acetic acid suspension in the presence of palladium-barium sulphate, forming *hydrobixin*, a thick, almost colourless oil containing one methoxyl group, which can be esterified by means of methyl-alcoholic hydrogen chloride to *hydromethylbixin*, a thick, pale yellow oil, b. p. 280—285°/18 mm., containing two OMe groups, which is also produced when methylbixin absorbs eighteen atoms of hydrogen, and is hydrolysed by means of methyl-alcoholic potassium hydroxide to *hydronorbixin*, a thick oil, b. p. 220—230°/13 mm., which acts as a dibasic acid on titration; this may be reconverted into hydromethylbixin by means of diazomethane or 3% methyl-

alcoholic hydrogen chloride. When hydromethylbixin is hydrolysed by means of alcoholic potassium hydroxide and the product oxidised by means of potassium permanganate, six atoms of oxygen seem to be taken up; the resulting *yellow oil*, apparently  $C_{25}H_{40}O_6$ , contains no methoxyl group. It is readily methylated by means of 3% methyl-alcoholic hydrogen chloride to an *oil*,  $C_{27}H_{40}O_6$ , containing two methoxyl groups.

When hydronorbixin is heated at  $320^\circ$ , carbon dioxide is eliminated, but no definite product has been isolated. Nevertheless, by the action of heat on a mixture of lime and the *calcium* salt of hydronorbixin under reduced pressure, an *oil* is produced approximately of the composition  $C_{23}H_{46}$ ; the presence of two carboxyl groups in hydronorbixin is therefore probable.

The hydrolysis of methylbixin to norbixin by means of methyl-alcoholic sodium hydroxide is demonstrated. No pure compound is obtained by the esterification of norbixin by means of concentrated methyl-alcoholic hydrogen chloride; the use of diazomethane leads, however, to the formation of methylbixin and to a small quantity of an isomeride,  $\beta$ -*methylbixin*, dark violet crystals, m. p.  $190-193^\circ$ , which is the sole product if 3% methyl-alcoholic hydrogen chloride is used. It is also formed by the action of diazomethane in ethereal solution on  $\beta$ -*bixin*, minute, bordeaux-red crystals, decomp.  $211-214^\circ$ , an isomeride of bixin which has been obtained during the preparation of bixin from a sample from Dutch Orleans. The existence of three isomeric monomethyl esters, bixin,  $\beta$ -bixin, and isobixin (Hasselt, *loc. cit.*), cannot be ascribed merely to the unsymmetrical position of the carboxyl groups in the norbixin molecule. It is suggested that the wandering of a double bond may underlie the change of structure which obviously must accompany the production of at least one of these isomerides.

W. S. N.

**New Pyrylium Salts.** C. GASTALDI and G. L. PEYRETH (*Gazzetta*, 1923, 53, i, 11-15).—Condensation of acetophenone or dypnone with propionic, butyric, and isovaleric anhydrides in presence of sublimed ferric chloride yields compounds analogous to that obtained under similar conditions from acetic anhydride (A., 1922, i, 573).

The *ferric chloride* compound of 4:6-diphenyl-2-ethylpyrylium chloride,  $FeCl_4 \cdot O \begin{smallmatrix} \text{C} \text{Et} \cdot \text{CH} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix} \gg \text{CPh}$ , formed from propionic anhydride, forms long, yellowish-brown needles, m. p.  $167^\circ$ , and yields a pale yellow aqueous solution showing slight green fluorescence. When treated in aqueous solution with excess of ammonia, it yields 4:6-diphenyl-2-ethylpyridine, the *nitrate* of which,  $C_{19}H_{15}O_2N_2$ , forms slender, colourless needles, m. p.  $180^\circ$  (decomp.). 4:6-Diphenyl-2-ethylpyrylium *nitrate*,  $C_{19}H_{17}O_2N$ , crystallises in pale yellow laminae, m. p.  $151^\circ$  (decomp.).

The *ferric chloride* compound of 4:6-diphenyl-2-propylpyrylium chloride,  $C_{20}H_{19}O \cdot FeCl_4$ , formed from butyric anhydride, forms greenish-yellow plates, m. p.  $197-198^\circ$ , and dissolves in concen-

ated sulphuric acid with blue fluorescence. 4:6-Diphenyl-propylpyridine nitrate,  $C_{20}H_{20}O_3N_2$ , crystallises in colourless needles, m. p.  $138^\circ$  (decomp.).

The ferric chloride compound of 4:6-diphenyl-2-isobutylpyrylium chloride,  $C_{21}H_{21}O \cdot FeCl_4$ , forms yellow prisms, m. p.  $165^\circ$ , and gives a pale yellow, aqueous solution showing slight blue fluorescence; the nitrate,  $C_{21}H_{21}O_4N$ , forms yellow prisms, m. p.  $156^\circ$ . 4:6-Diphenyl-2-isobutylpyridine nitrate,  $C_{21}H_{22}O_3N_2$ , crystallises in colourless needles, m. p.  $124^\circ$ .  
T. H. P.

**A Synthesis of Pyrylium Salts of Anthocyanidin Type. II.**  
DAVID DOIG PRATT and ROBERT ROBINSON (T., 1923, 123, 745—58).

**A Direct Synthesis of certain Xanthylium Derivatives.**  
DAVID DOIG PRATT and ROBERT ROBINSON (T., 1923, 123, 739—45).

**Anhalonium Alkaloids. V. Synthesis of Anhalonidine and Pellotine.** ERNST SPÄTH (*Monatsh.*, 1923, 43, 477—484).—By the action of cold, concentrated hydrochloric acid on  $\beta$ -5-benzylxy-3:4-dimethoxyphenylethylamine (A., 1922, i, 852), the benzyl group is removed. Acetic anhydride converts the product into the *O,N*-diacetyl derivative, which, when heated in toluene solution with phosphoric oxide, gives a base which, from its mode of formation, must be either 6-acetoxy-7:8-dimethoxy- or 8-acetoxy-6:7-dimethoxy-1-methyl-3:4-dihydroisoquinoline, and on reduction with tin and hydrochloric acid gives a substance identical in all respects with anhalonidine. This alkaloid must therefore be either 6-hydroxy-7:8-dimethoxy- or 8-hydroxy-6:7-dimethoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline. The former constitution accords the better with that of anhalamine, and is more probable on the grounds that the above ring-closure would be more likely to occur in the para-position to an acetoxy-group than in the similar position with respect to a methoxy-group.

By the addition of methyl iodide to the above dihydroisoquinoline derivative, and reduction of the product with tin and hydrochloric acid (the second process effecting also hydrolysis of the *O*-acetyl group), pellotine (i.e., *N*-methylanhalonidine) is obtained.

The great reactivity, with aldehydes, of the above-mentioned ethylamine derivative suggests that neither anhalonidine nor pellotine is formed in the plant as a result of enzyme action. The lability of groups attached to the asymmetric carbon atom in position 1, caused by the (probable) presence of a hydroxyl group in position 6, may explain the optical inactivity of the two natural alkaloids.  
E. E. T.

**Echinopsine.** ERNST SPÄTH and ALFRED KOLBE (*Monatsh.*, 1923, 43, 469—475).—This alkaloid, to which Greshoff (A., 1901, i, 338) erroneously assigned the formula  $C_{11}H_9ON$ , is identical with 1-methyl-4-quinolone,  $C_{10}H_9ON$ , obtained in an impure condition

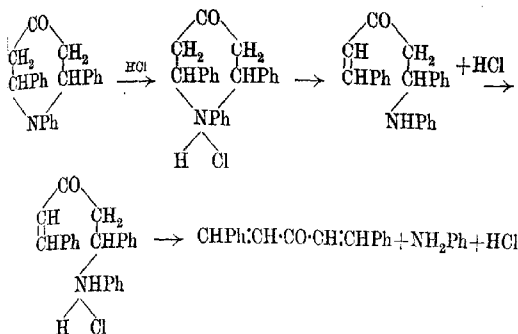
by Meyer (A., 1906, i, 604). On reduction, either with sodium and alcohol, or electrolytically, echinopsine is converted into 1-methyltetrahydroquinoline, whilst when heated with a mixture of phosphorus penta- and oxy-chlorides it is converted into 4-chloroquinoline. From the latter, quinoline is obtained by reducing with hydrogen in presence of palladium and barium sulphate. The alkaloid is readily obtained by heating 4-hydroxyquinoline with methyl iodide and sodium methoxide, and gives a *hydrochloride*, m. p. 185–186°, and a *picrate*, m. p. 223–224°. E. E. T.

**Preparation of Ergotamine Salts.** CHEMISCHE FABRIK VORN. SANDOZ (Brit. Pat. 170302).—Ergotamine salts are obtained in crystalline form by the action of the requisite amount of acid on the free base dissolved in an organic solvent miscible with water, such as methyl or ethyl alcohol, acetone, etc., whereby separation of the salt occurs almost immediately. The preparation of two sulphates in this way, containing 10.36% and 7.56%  $\text{H}_2\text{SO}_4$  respectively, is described. On recrystallisation, the former passes into the latter by loss of sulphuric acid. These and other ergotamine salts retain solvent of crystallisation very tenaciously. Salts containing a minimum amount of acid are obtained by shaking an ergotamine solution in a non-miscible organic solvent such as chloroform, with gradually increasing quantities of the acid. The precipitate is collected and recrystallised from methyl alcohol. In this way, a *hydrochloride* in the form of thin prisms containing, after drying to constant weight, 5.85%  $\text{HCl}$ , was obtained. The preparation of the tartrate in the form of compact prisms from ethyl alcohol, and of the citrate and carbonate in physiological sodium chloride solution, is also described. The ergotamine salts and their solutions are easily oxidised by air, particularly in sunlight, becoming thereby yellow or brown. Access of air should therefore be prevented during the preparation and storage of these compounds. G. F. M.

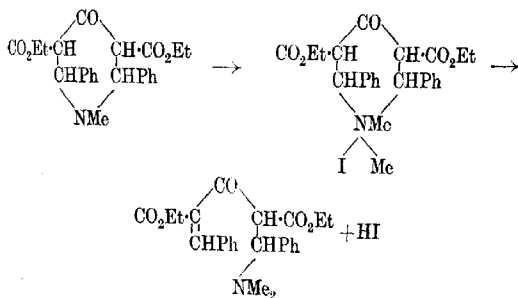
**Physostigmine. I. Alkylation Products of Eseroline.** GEORGE BARGER and EDGAR STEDMAN (T., 1923, 123, 758–769).

**Some Pyridine Derivatives of Iridium.** MARCEL DÉLÉPINE (*Ann. Chim.*, 1923, [ix], 19, 5–31).—A more detailed account of work already published (cf. A., 1922, i, 859; 1923, i, 89, 135, 243). H. J. E.

**A Reaction Involving the Rupture of the Ring in Heterocyclic Compounds. I.** P. PETRENKO-KRITSCHENKO, E. PUTIATA, and A. GANDELMAN (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1852–1861).—The action of hydrogen chloride and of methyl iodide on some substituted 4-piperidones is investigated. Hydrogen chloride is passed through a benzene solution of 1 : 2 : 6-triphenyl-4-piperidone. The hydrochloride thus precipitated is treated with alkali, which liberates distyryl ketone and aniline. This reaction is thus explained :



The case with which the ring is broken in this compound is due to the close proximity of the three phenyl groups, as the corresponding N-methyl compound when treated in the same way regenerates the same compound. It appears also that the triphenyl derivative can be stabilised by converting the grouping  $-\text{CH}_2\text{COCH}_2-$  into  $-\text{CHR}\cdot\text{CO}\cdot\text{CHR}-$ , where R is a carbethoxy-group. The action of methyl iodide on ethyl 2:6-diphenyl-1-methyl-4-piperidone-3:5-dicarboxylate is next examined. The hydriodide of this ester is prepared by the action of methyl iodide on the corresponding ester of diphenylpiperidonedicarboxylic acid, and the free 1-methyl ester, m. p.  $85^\circ$ , is obtained from it by the action of weak ammonia. Prolonged boiling of this substance with methyl iodide merely results in the formation of its hydriodide. The formation of this salt is explained as follows:



The hydrogen iodide thus liberated combines with unacted on 1-methyl ester to form its hydriodide. No other product was isolated from the reaction mixture. Hydrogen chloride passed through a benzene solution of this ester gives a variety of products, of which only one is identified as the stereoisomeride, m. p.  $138^\circ$ ,

of the original substance, m. p. 85°. The action of methyl iodide on *N*-methyltriacetoneamine is to cause rupture of the ring. The latter substance is preparable by the action of methyl iodide on triacetoneamine, thus showing that the view held up to the present, that the homologues of the latter substance cannot be prepared by direct alkylation, is incorrect.

R. T.

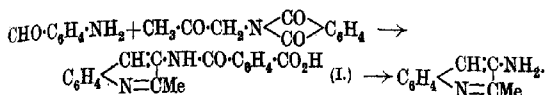
**Influence of Solvents on the Grignard Reactions.** RIKO MAJIMA and MUNIO KOTAKE (*J. Chem. Soc. Japan*, 1922, 43, 936-948; cf. this vol., i, 495).—The influence of solvents (ethyl ether and anisole) in the Grignard reaction between magnesium indole iodide and the following has been studied, with results which may be summarised as follows:

| Reagent.                     | Reaction products.            | Yields          |             |
|------------------------------|-------------------------------|-----------------|-------------|
|                              |                               | In ethyl ether. | In anisole. |
| Formic ester . .             | indole-2-aldehyde             | trace           | 33%         |
| Carbon dioxide . .           | indole-2-carboxylic acid      | 8.6%            | 25%         |
| Acetone . . . .              | 2-indolyldimethylmethane      | 22.5%           | 30.4%       |
| Benzaldehyde . .             | di-2-indolylphenylmethane     | 20%             | 61.6%       |
| Chloroformic ethyl ester . . | ethyl indole-2-carboxylate    | 53.5%           | 38.7%       |
| Acetyl chloride . .          | 2-indolyl methyl ketone       | 93%             | 61%         |
| Chloroacetyl chloride . .    | 2-indolyl chloromethyl ketone | 45%             | 4.8%        |

From the results, the authors have drawn the conclusion that when a compound having a carbonyl group acts on magnesium indole iodide, a good yield is obtained by using anisole as a solvent; whilst if the reacting compound is an acid chloride, ethyl ether is a better solvent.  $\beta$ -Indolylchloromethyl ketone forms colourless, rhombic crystals, m. p. 212–214°. K. K.

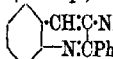
**3-Amino- and 3-Hydroxy-quinolines.** G. BARGELLINI and S. BERLINGOZZI (*Gazzetta*, 1923, 53, i, 3–11).—The authors have prepared 3-hydroxy-2-phenylquinoline by the action of *o*-aminobenzaldehyde on either *o*-bromoacetophenone or benzoylcarbinol, and 3-hydroxy-2-*p*-anisylquinoline from chloroacetanisole and *o*-aminobenzaldehyde, the action of ketones containing the group  $\cdot\text{CO}\cdot\text{CH}_2\text{X}$  (X=a halogen atom) on *o*-aminobenzaldehyde in presence of sodium hydroxide constituting a general method for the preparation of 3-hydroxyquinolines. Similar condensations occur if the *o*-aminobenzaldehyde is replaced by one of its derivatives or by isatin or an *o*-amino-ketone.

3-Aminoquinoline derivatives have been prepared by complicated series of reactions (Stark, A., 1907, i, 973; Mills and Watson, T., 1910, 97, 741), but no general method is known. The authors find that 3-amino-2-methylquinoline is readily prepared by condensing *o*-aminobenzaldehyde with acetonylphthalimide in presence of sodium hydroxide and decomposing the compound formed by boiling it with 20% hydrochloric acid:



3-Amino-2-phenylquinoline may be obtained similarly from *o*-aminobenzaldehyde and phenacylphthalimide. The formation of 3-nitroquinoline from *o*-aminobenzaldehyde and methazonic acid (Badische Anilin- & Soda-Fabrik, A., 1921, i, 517) is analogous to the method described above, since methazonic acid reacts as the oxime of nitroacetaldehyde.

The compound  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$  (formula I, above) forms silky, yellow needles, m. p.  $220^\circ$  (decomp.).

The compound  prepared from

*o*-aminobenzaldehyde and phenacylphthalimide, forms white scales, m. p.  $205-206^\circ$  (decomp.).

3-Amino-2-phenylquinoline,  $\text{C}_{17}\text{H}_{13}\text{N}_2$ , crystallises in pale yellow needles, m. p.  $115-116^\circ$ , and dissolves in acids, giving intensely fluorescent solutions. Its *acetyl* derivative forms colourless needles, m. p.  $173-175^\circ$ , and its *picrate*, yellow prisms, m. p.  $194-195^\circ$ .

3-Hydroxy-2-phenylquinoline,  $\text{C}_{16}\text{H}_{11}\text{ON}$ , prepared either by diazotisation of 3-amino-2-phenylquinoline or by the action of *o*-bromoacetophenone or benzoylcarbinol on *o*-aminobenzaldehyde (cf. Koenigs and Stockhausen, A., 1902, i, 693), forms white needles, m. p.  $221-222^\circ$ , and yields fluorescent aqueous and alcoholic solutions, the latter giving a reddish-brown coloration with ferric chloride. The *hydrochloride* forms lustrous, yellow scales, m. p.  $243-245^\circ$ ; the *chloroplatinate*, orange-yellow crystals, blackening above  $260^\circ$ ; the *picrate*, yellow prisms, m. p.  $235-238^\circ$  (decomp.); the *sulphate*, yellow leaflets, turning brown at  $150^\circ$  and melting indistinctly at about  $165^\circ$ .

3-Hydroxy-2-*p*-anisylquinoline,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$ , crystallises in white needles, m. p.  $240-242^\circ$  (decomp.). The *sulphate*, yellow needles, m. p.  $225-230^\circ$  (decomp.), *hydrochloride*, *chloroplatinate*, and *picrate*, m. p.  $216-228^\circ$ , were prepared. T. H. P.

**$\gamma$ -Chloropropyl Urethanes and a Synthesis of the 1:3-Oxazine Ring.** ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1923, 45, 723-727).— $\gamma$ -Chloropropyl alcohol reacts readily with carbonyl chloride in ice-cold toluene solution to give  *$\gamma$ -chloropropyl chloroformate*, b. p.  $175-176^\circ/736$  mm., which, when heated with carbamide (2 mols.), gives  *$\gamma$ -chloropropyl allophanate*, white, scaly crystals, m. p.  $166^\circ$ .  *$\gamma$ -Chloropropyl carbamate*, white, pearly scales, m. p.  $62^\circ$ , is formed when  $\gamma$ -chloropropyl alcohol and carbamide nitrate (2 mols.) are heated together at  $130-135^\circ$ , or, in better yield (71%), when the chloroformate is slowly dropped into ice-cold 10% aqueous ammonia (2 mols.). Attempts to prepare an oxazine by the elimination of hydrogen chloride from the above carbamate were unsuccessful; the action of aqueous sodium hydroxide leads to hydrolysis, whilst with alcoholic sodium

ethoxide sodium cyanate and phenylcarbamide are produced.  $\gamma$ -Chloropropyl chloroformate reacts with aniline in ice-cold ethereal solution giving  $\gamma$ -chloropropyl phenylcarbamate, long, flat prisms, m. p.  $38^\circ$ , b. p.  $160$ — $170^\circ/5$  mm., which is also produced when chloropropyl alcohol and phenylcarbimide are gradually heated together at  $150^\circ$ ; the action of boiling aqueous-alcoholic sodium hydroxide on the carbanilate leads to 2-keto-3-phenyltetrahydro-1:3-oxazine, large, thick prisms, m. p.  $96^\circ$ , yield 84%. Chloropropyl chloroformate reacts in cold ethereal solution with o-toluidine to give  $\gamma$ -chloropropyl o-tolylcarbamate, small needles, m. p.  $49^\circ$ , b. p.  $170$ — $175^\circ/5$  mm., from which, by the elimination of hydrogen chloride, 2-keto-3-o-tolyltetrahydro-1:3-oxazine, large, flat prisms, m. p.  $89^\circ$ , is produced in 60% yield.

The formation of the 6-membered 1:3-oxazine ring is analogous to that of the 5-membered 1:3-oxazole ring, by the elimination of hydrogen chloride from  $\beta$ -halogen carbanilates (Otto, A., 1891, 1373; Johnson and Langley, A., 1910, i, 884). W. S. N.

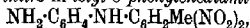
**Tetrahydro-1:3:2-oxazones and Substituted  $\gamma$ -Aminopropanols.** J. S. PIERCE and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 790—795; cf. this vol., i, 457).— $\gamma$ -Chloropropyl arylcarbamates are formed in aqueous suspension from aromatic amines and  $\gamma$ -chloropropyl chloroformate.  $\gamma$ -Chloropropyl arylcarbamates are converted by alcoholic potash (1 mol.) into tetrahydro-1:3:2-oxazones; if 4 mols. of alkali are used,  $\gamma$ -arylaminoopropanols are produced.

The following compounds are described:  $\gamma$ -Chloropropyl o-tolylcarbamate, white needles, m. p.  $46$ — $46.5^\circ$ , b. p.  $182.5^\circ/4.5$  mm.  $\gamma$ -Chloropropyl phenylcarbamate, white needles, m. p.  $35$ — $36^\circ$ , b. p.  $190^\circ/3.5$  mm.  $\gamma$ -Chloropropyl p-tolylcarbamate, b. p.  $188^\circ/4.5$  mm.  $\gamma$ -Chloropropyl o-chlorophenylcarbamate, b. p.  $178.5^\circ/3.5$  mm.  $\gamma$ -Chloropropyl p-chlorophenylcarbamate, white needles, m. p.  $53$ — $53.5^\circ$ , b. p.  $193^\circ/5$  mm.  $\gamma$ -Chloropropyl p-anisylcarbamate, white needles, m. p.  $63$ — $63.5^\circ$ , b. p.  $198.5^\circ/4$  mm.  $\gamma$ -Chloropropyl p-carboxyphenylcarbamate, white crystals, m. p.  $191$ — $192.5^\circ$ .  $\gamma$ -Chloropropyl  $\alpha$ -naphthylcarbamate, white needles, m. p.  $75.5$ — $76.5^\circ$ , b. p.  $206.5^\circ/4$  mm. 3-Phenyltetrahydro-1:3:2-oxazone, white plates, m. p.  $94$ — $94.5^\circ$ . 3-o-Tolyltetrahydro-1:3:2-oxazone, white prisms, m. p.  $87$ — $87.5^\circ$ . 3-p-Tolyltetrahydro-1:3:2-oxazone, white needles, m. p.  $127.5$ — $128^\circ$ . 3-o-Chlorophenyltetrahydro-1:3:2-oxazone, white cubes, m. p.  $99^\circ$ . 3-p-Chlorophenyltetrahydro-1:3:2-oxazone, white plates, m. p.  $111.5$ — $112^\circ$ . 3-p-Ethoxyphenyltetrahydro-1:3:2-oxazone, white plates, m. p.  $112.5$ — $113^\circ$ . 3-p-Carboxyphenyltetrahydro-1:3:2-oxazone, white plates, m. p.  $231$ — $232^\circ$ . 3- $\alpha$ -Naphthyltetrahydro-1:3:2-oxazone, white needles, m. p.  $149.5$ — $150.5^\circ$ .  $\gamma$ -Anilinopropyl alcohol, b. p.  $180.5^\circ/20.5$  mm. or  $154^\circ/5$  mm.  $\gamma$ -o-Toluidinopropyl alcohol, b. p.  $184^\circ/3$  mm.  $\gamma$ -p-Toluidinopropyl alcohol, b. p.  $163.5^\circ/3.5$  mm.  $\gamma$ -o-Chloroanilinopropyl alcohol, b. p.  $151.5^\circ/3.5$  mm.  $\gamma$ -p-Chloroanilinopropyl alcohol, b. p.  $167^\circ/3.5$  mm.  $\gamma$ -p-Phenetidinopropyl alcohol, white plates, m. p.  $42$ — $42.5^\circ$ , b. p.  $177^\circ/3.5$  mm.  $\gamma$ -p-Carboxyanilinopropyl alcohol, white

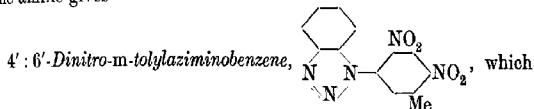
needles, m. p. 151—152°.  $\gamma$ - $\alpha$ -Naphthylaminopropyl alcohol, a yellow oil, b. p. 201.5°/3.5 mm. W. S. N.

**Reactions of Thiosemicarbazones. II. Action of Esters of  $\alpha$ -Halogenated Acids.** FORSYTH JAMES WILSON and ROBERT BURNS (T., 1923, 123, 799—804).

**The Action of Phenylenediamines on  $\beta$ - and  $\gamma$ -Trinitrotoluenes.** MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1923, 53, i, 49—52).—4' : 6'-Dinitro-*m*-tolyl-*o*-phenylenediamine,



prepared by the interaction of 2 : 4 : 6-trinitrotoluene (1 mol.) and *o*-phenylenediamine (2 mols.) in alcoholic solution, crystallises in orange-yellow needles, m. p. 195—196°, dissolves in concentrated sulphuric acid with yellow coloration, and, in alcoholic solution, gives a deep red coloration with alkalis. With benzaldehyde it yields the *benzylideneimine*,  $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_4$ , which forms lustrous, red prisms, m. p. 214—215°, and gives a red coloration with concentrated sulphuric acid. The *acetyl* derivative of the amine,  $\text{C}_{13}\text{H}_{14}\text{O}_5\text{N}_4$ , forms pale yellow prisms, m. p. 222—223°, and, in alcoholic solution, yields a red coloration with alkali. The action of nitrous acid on the amine gives

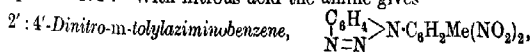


forms lustrous, white laminae, m. p. 164—165°, and, in alcoholic solution, gives a blue coloration with excess of alkali.

4' : 6'-Dinitro-*m*-tolyl-*m*-phenylenediamine,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_4$ , prepared from 2 : 4 : 6-trinitrotoluene and *m*-phenylenediamine, crystallises in lustrous, reddish-yellow needles, m. p. 160—161°, gives a reddish-yellow solution in concentrated sulphuric acid, and, in alcoholic solution, gives a deep red coloration with alkali. Its *acetyl* derivative forms reddish-yellow prisms, m. p. 224—225°, and gives a dark red coloration with alkali in alcoholic solution.

4' : 6'-Dinitro-*m*-tolyl-*p*-phenylenediamine, obtained from 2 : 4 : 5-trinitrotoluene (1 mol.) and *p*-phenylenediamine, crystallises in long, garnet-red needles, m. p. 174—175°, yields a red solution in concentrated sulphuric acid, and, in alcoholic solution, forms a deep red coloration with alkali. The *acetyl* derivative separates in reddish-yellow, silky needles, m. p. 222—223°.

2' : 4'-Dinitro-*m*-tolyl-*o*-phenylenediamine, prepared from 2 : 3 : 4-trinitrotoluene and *o*-phenylenediamine, crystallises in lustrous, garnet-red needles, m. p. 149—150°, dissolves in concentrated sulphuric acid to a reddish-yellow solution, and, in alcoholic solution, gives a deep red coloration with alkali; it forms a pasty, golden-yellow *acetyl* compound. With benzaldehyde, it yields the *benzylideneimine*,  $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_4$ , which forms lustrous, red prisms, m. p. 173—174°. With nitrous acid the amine gives



which crystallises in lustrous, white prisms, m. p. 156—157°, and, in alcoholic solution, gives with alkali a violet coloration changing immediately to blue.

2' : 4'-Dinitro-m-tolyl-p-phenylenediamine, prepared from 2 : 3 : 4-trinitrotoluene and p-phenylenediamine, crystallises in lustrous, garnet-red needles, m. p. 174—175°.

T. H. P.

**Application of the Hofmann Reaction to Substituted Carbamides.** GEORGE ROBERT ELLIOTT (T., 1923, 123, 804—813).

**The Action of Sodamide on Pyridine, with some Observations on 2-Aminopyridine and some of its Derivatives.** J. P. WIBAUT and ELISABETH DINGEMANSE (*Rec. trav. chim.*, 1923, 42, 240—250; *Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 458—462; cf. Tschitschibabin and Zeide, A., 1915, i, 590).—The action of sodamide on pyridine results in formation of 2-aminopyridine, 4 : 4'-dipyridyl, and dipyridylamine, but 2 : 6-diaminopyridine and 4-aminopyridine were not detected. A study of the action of oxidising agents on 2-aminopyridine showed that it rapidly decolorises alkaline permanganate, has little action on alkaline chromate, and slowly reduces acid chromate solution. The oxidation products were not isolated.


2-Acetamidopyridine forms monoclinic prisms ( $a : b : c = 1.4939 : 1 : 2.0719$ ,  $\beta = 89^\circ 14' 30''$ ); 2-aminopyridylurethane crystallises in the monoclinic prismatic system ( $a : b : c = 0.7946 : 1 : 1.3552$ ,  $\beta = 73^\circ 21'$ ).

H. J. E.

**The Hydrolysis of the Xanthyl Derivatives of Veronal and Hypnotics of the Barbituric Acid Series, and its Importance in Toxicology.** RENÉ FABRE (*J. Pharm. Chim.*, 1923, [vii], 27, 337—339).—The xanthyl derivatives of veronal and other alkyl-barbituric acids, the preparation and use of which in toxicological investigations has previously been described (A., 1922, ii, 795), are readily hydrolysed by boiling for one hour with 20% alcoholic hydrogen chloride, and the original barbituric acid is recoverable from the reaction product in almost theoretical yield by rendering alkaline, extracting insoluble matter by means of ether, acidifying the alkaline solution, and extracting once more with ether. On evaporating the rather ethereal extract, the barbituric acid is obtained in pure crystalline form.

G. F. M.

**The Synthesis of Iminazolyglycine [Glyoxalineaminoacetic Acid]. The Lower Homologue of Histidine.** CORBET PAGE STEWART (*Biochem. J.*, 1923, 17, 130—133).—4(or 5)-Hydroxymethylglyoxaline, obtained from citric acid, was oxidised to the glyoxaline-4(or 5)-formaldehyde. The latter compound was converted by the treatment with potassium cyanide and ammonium chloride into the amino-nitrile, which was eventually hydrolysed to the amino-acid. The hydrochloride of the compound was found to be hygroscopic and decomposed when attempts were made to dry it at 100°. The picolonate, m. p. 243° (uncorr.), was prepared in order to purify the crude product obtained by the above method. Glyoxalineaminoacetic acid forms a condensation compound with

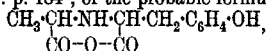
2:3:4-trinitrotoluene,  $\text{NH}\cdot\text{CH}=\text{C}\cdot\text{CH}\cdot\text{NH}\cdot\text{CO}_2\text{H}$  , the 3-nitro-group disappearing in the condensation; it forms deep yellow crystals, decomp. 270°. S. S. Z.

**Synthesis of Polypeptide Hydatoints. Tyrosyl-Alanine Hydatoint.** DOROTHY A. HAHN, LOUISE KELLEY, and FLORENCE SCHAEFFER (*J. Amer. Chem. Soc.*, 1923, 45, 843—857).—The alkylation of 4-*p*-anisylidenehydantoin and of 4-anisylhydantoin by means of ethyl  $\alpha$ -bromopropionate has been investigated; the ester group enters the position 3, in contrast to the behaviour of ethyl chloroacetate, which becomes attached to nitrogen in the position 1 (cf. A., 1916, i, 504; 1917, i, 475).

The action of sodium ethoxide and ethyl  $\alpha$ -bromopropionate on 4-*p*-anisylidenehydantoin leads to ethyl 4-*p*-anisylidenehydantoin-3- $\alpha$ -propionate, which exists in stereoisomeric forms, (a) large, glistening plates, m. p. 143°; (b) long, fine, white, felted needles, m. p. 176°; both forms of the ester are hydrolysed by means of hydrochloric acid, yielding corresponding forms of 4-*p*-anisylidenehydantoin-3- $\alpha$ -propionic acid,  $\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{OMe})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , (a) hard, white needles or plates, m. p. 245°; (b) hard, white needles or plates, m. p. 269°. Either form of the ester, preferably the less fusible modification, is reduced by means of sodium amalgam in alcoholic solution to ethyl 4-*p*-methoxybenzylhydantoin-3- $\alpha$ -propionate, long, fine, white needles, or plates, m. p. 138°, which is also produced by the action of sodium ethoxide and ethyl  $\alpha$ -bromopropionate on 4-*p*-methoxybenzylhydantoin. This ester is converted by the action of alcoholic sodium hydroxide into the sodium salt, crystalline, of 4-*p*-methoxybenzylhydantoin-3- $\alpha$ -propionic acid, hard, white prisms, m. p. 164—166°, which is also formed by the action of concentrated hydrochloric acid on *N*-carbamyl-5-*p*-methoxyphenyl- $\alpha$ -iminodipropionic acid,

$\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{N}(\text{CO}\cdot\text{NH}_2)\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , glistening, white plates, m. p. 148—149°, decomp. The latter is formed as its disodium salt, m. p. 240°, decomp., by the action of ethyl-alcoholic sodium ethoxide (2 mols.) on ethyl 4-*p*-methoxybenzylhydantoin-3- $\alpha$ -propionate. 4-*p*-Hydroxybenzylhydantoin-3- $\alpha$ -propionic acid, rosettes of hard, compact crystals, m. p. 217°, ethyl ester, long, felted needles, m. p. 192°, is formed by the action of hydriodic acid and red phosphorus at 100—110° on either form of 4-*p*-anisylidenehydantoin-3- $\alpha$ -propionic acid, either form of its ethyl ester, 4-*p*-methoxybenzylhydantoin-3- $\alpha$ -propionic acid, or its ethyl ester. When 4-*p*-hydroxybenzylhydantoin-3- $\alpha$ -propionic acid is heated for four hours at 155° with concentrated hydrochloric acid, it is converted into 4-methylhydantoin-3- $\alpha$ -*p*-hydroxyphenylpropionic acid,  $\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{CHMe})\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 221°, by an intramolecular rearrangement, probably involving the addition and subsequent elimination of the elements of water. The action

of concentrated hydriodic acid and red phosphorus at 180° or 4-*p*-hydroxybenzylhydantoin-3- $\alpha$ -propionic acid leads to a crystal line substance, m. p. 184°, of the probable formula,



and ammonia; the production of ammonia in this experiment, and the interconversions described, are clear proof that the propionic residue enters in the position 3 during the original alkylations.

W. S. N.

**Fluorindinium Salts.** F. KEHRMANN and PETER LEUZINGER (*Helv. Chim. Acta*, 1923, 6, 239—248).—By the action of methyl sulphate on diphenylphenofluorindine bases (cf. A., 1896, i, 512), basic dyes are formed, which are stable to alkalis and have the properties of ammonium salts. A number of such

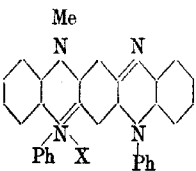
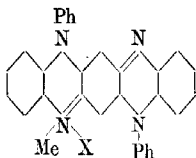
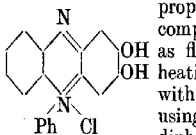
compounds have been prepared and characterised as fluorindinium salts. It was found that, by heating hydroxyaposafranone (annexed formula), with *o*-aminodiphenylamine or its hydrochloride, using benzoic acid as solvent, only the green isodiphenylphenofluorindine was formed, unaccom-

panied by the red diphenylphenofluorindine. The constitution of

diphenylmethylphenofluorindinium monoacid salts is expressed by the accompanying formula, where X is the acid radicle. *Diphenylmethylphenofluorindinium perchlorate*,  $\text{C}_{31}\text{H}_{23}\text{O}_4\text{N}_4\text{Cl}$ , crystallises in bronze needles, and the *di-perchlorate* forms bright, brassy needles. Both are practically insoluble in water, but soluble in boiling 80—90% alcohol.

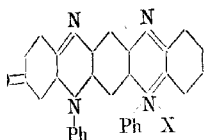
The colour in concentrated sulphuric acid is greenish-blue with a strong red fluorescence, not changing on dilution, but becoming pure blue when the free acid is neutralised. Cold alkali hydroxide does not change the colour of the alcoholic solution, but on warming the colour becomes reddish-violet with a fiery red fluorescence, through hydrolysis of the methyl group. Aqueous solutions of phenofluorindinium salts have an intensely bitter taste, whilst salts of diphenylphenofluorindine are tasteless. Ethyl sulphate reacts more slowly than methyl sulphate with diphenylphenofluorindine in nitrobenzene solution. *Diphenylethylphenofluorindinium diperchlorate* resembles the lower methyl homologue; the reactions are similar but decomposition of the ammonium base by alkali is considerably slower.

The constitution of salts of isodiphenylmethylphenofluorindinium may be expressed by the annexed formula, although alternatives are possible. *isoDiphenylmethyl(ethyl)phenofluorindinium mono- and di-perchlorates* resemble closely the isomeride described above. When the bases are warmed with alkali in alcoholic solution, an olive-green colour quickly develops, but this green is not due to formation of



isodiphenylphenofluorindine, since it slowly changes to a reddish-violet with a strong red fluorescence. The nature of these changes is not yet been determined.

When isodiphenylphenofluorindine is oxidised with chromic acid, the reaction cannot be stopped at the di-phenazonium stage, but proceeds to the formation of a fluorindinone, corresponding closely with the oxidation of phenylphenazonium salts to aposafranone by



air. *isoDiphenylphenofluorindinone perchlorate*, annexed formula,  $C_{30}H_{19}O_3N_4Cl$ , forms small, green needles with a brassy reflex, dissolving in 80% alcohol with a permanganate-red colour, unaltered by ammonia or carbonate, but changing to orange-yellow with sodium hydroxide.

In concentrated sulphuric acid it has yellowish-green colour, becoming violet-red on dilution. When reduced in alcohol with stannous chloride, it becomes intensely bluish-green, probably due to the formation of a *hydroxyisodiphenylphenofluorindine* salt. This is reoxidised by ferric chloride. The perchlorate forms fairly large brassy crystals, and the *chloroplatinate*,  $(C_{30}H_{19}ON_4)_2PtCl_6$ , a heavy, greenish-grey, metallic, microcrystalline powder.

E. H. R.

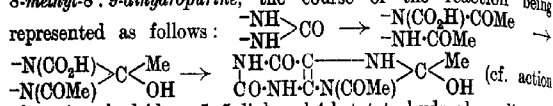
**Solubility of Uric Acid in Water.** HEINRICH BILTZ and ESBET HERBERMANN (*Annalen*, 1923, 431, 104—111).—It is shown that the supersaturation which occurs (cf. A., 1921, i, 606, 609; also Chad and Boden, A., 1913, i, 403) when a warm aqueous solution of uric acid is allowed to cool to room temperature in contact with solid uric acid is probably the cause of the high values for the solubility found by Bensch (*Annalen*, 1845, 54, 190) and Behrend and Roosen (*Annalen*, 1889, 251, 250). A true equilibrium is, however, slowly reached when a cooled supersaturated solution is shaken, or, more rapidly, when solution is effected by shaking the solid acid with water at the room temperature; the values for the solubility found in this way agree with the figures of His and Paul (A., 1901, i, 131; cf. Kohler, A., 1911, i, 690). The observation of His and Paul, that the solubility increases with the time of shaking, has not been confirmed, but it is agreed that saturation is quickly attained.

In these experiments, solution is effected in vessels of Jena glass, the concentrations being determined by evaporation of the filtered liquid in a platinum dish. After weighing, the basin and contents are brought to a red heat, cooled, and re-weighed, to determine the soluble matter present in the solution, derived from the glass. Incidentally, the stability of uric acid and of 3:9-dimethyluric acid to water is demonstrated by means of measurements of hydrogen-ion concentration.

W. S. N.

**Action of Acetic Anhydride on Uric Acid.** HEINRICH BILTZ and WALTER SCHMIDT (*Annalen*, 1923, 431, 70—104).—During the preparation of 8-methylxanthine by the action of acetic anhydride on uric acid (A., 1902, i, 125), Boehringer & Söhne isolated an intermediate product (A., 1902, i, 504) which they described as

2:4-dioxy-5:6-diacetamidopyrimidine; this could undoubtedly give 8-methylxanthine by elimination of acetic acid. Since, however, only one acetyl group can be eliminated by hydrolysis, it is now suggested that this intermediate product, the preparation of which is described, is to be formulated as 9-acetyl-2:6:8-trioxy-8-methyl-8:9-dihydropurine, the course of the reaction being represented as follows:



of acetic anhydride on 5:5-diphenyl-4-ketotetrahydroglyoxaline, A., 1922, i, 871). If ring formation occurs before the elimination of the carboxyl group, the process is comparable with the formation of carbinols from orthodiamines (Fischer, A., 1901, i, 413; 1902, i, 188). It is shown that the formula also agrees with the other properties of the substance.

Hydrolysis by means of aqueous sodium hydroxide or of fuming hydriodic acid leads to 2:6:8-trioxy-8-methyl-8:9-dihydropurine, which forms tabular prisms, decomp. above 300°, and yields an amorphous silver salt, a perchlorate, decomp. 163—164°, a sulphate, hydrochloride, and nitrate, and also a potassium salt, ciliate needles, which reacts with benzoyl chloride, giving a benzoyl derivative (? benzoate), very small leaflets of high melting point. Trioxymethyldihydropurine gives alloxan when oxidised by means of chlorine water. Trioxymethyldihydropurine, or its acetyl derivative, when heated with acetic anhydride loses water, or acetic acid, with formation of 8-methylxanthine, identical with Boehringer & Söhne's product, after the latter has been purified (details given) through the potassium salt; the perchlorate, colourless, tabular crystals, decomp. 292—294°, hydriodide, large, tabular crystals, sulphate, long, slender, four-sided prisms, mononitrate, small crystals, and the dinitrate, slender needles, are described. The reduction of trioxymethyldihydropurine by means of hydriodic acid, or, as a side-reaction, the hydrolysis of the acetyl derivative by the same reagent, leads to 8-methyl-8:9-dihydroxanthine, small, colourless, transparent leaflets of high melting point, hydriodide, small, glistening six-sided tablets, decomp. indefinitely.

The methylation of trioxymethyldihydropurine by means of methyl sulphate leads to 2:6:8-trioxy-3:8-dimethyl-8:9-dihydropurine, long, slender needles, decomp. 305—306°, in which the second methyl group is attached to nitrogen, since no methoxyl is removable by means of hydriodic acid. That the methyl group is in position 1 or 3 is shown by the production, when oxidised with chlorine water, of a product which gives methylvioluric acid monohydrate on treatment with hydroxylamine acetate. The structure of the above dimethyl compound is finally proved by the production, by the action of acetic anhydride and a little pyridine, of 3:8-dimethylxanthine (A., 1902, i, 125), the constitution of which is now fixed beyond doubt by its synthesis from acetic anhydride and a sample of 3-methyluric acid (A., 1919, i, 292, 293) absolutely free from 9-methyluric acid.

2:4-Dioxy-5:6-diaminopyrimidine (Traube, A., 1900, i, 389), the preparation of which is described, gives a *sodium* salt, small, faintly yellowish-brown leaflets, which with hydrochloric acid gives a *hydrochloride*, pale yellow crystals, decomp. 253—255°; a *nitrate* has also been prepared. The action of acetic anhydride and a little pyridine on the above sodium salt leads to 2:6:8-trioxy-1:9-diacetyl-8-methyl-8:9-dihydropurine, small, brown prisms of high melting point, probably identical with the product described by Boehringer & Söhne (*loc. cit.*) as triacetyldiaminouracil; the *monohydrate* of a *sodium* salt of the same compound, slender needles, decomp. 258—260°, is also formed. The latter gives the 9-acetyl derivative on partial hydrolysis by means of sodium hydroxide; both the diacetyl compound and the sodium salt give trioxymethyl-dihydropurine on prolonged alkaline hydrolysis. W. S. N.

**Reactions of Diazonium Salts with Cupric Compounds. I.**  
A. CONTARDI (*Ann. Chim. Appl.*, 1923, 7, 13—28).—Previous work on the transformations of diazo-compounds, especially those effected with the help of cupric salts, is discussed, and a table is given showing, for forty different amino-derivatives, the compounds obtained when the corresponding diazo-salts are treated with cupric chloride (or bromide) or sodium or cupric nitrite, and also those obtained when the diazophenols are treated with cupric chloride or bromide. Considerations of these results leads to the following generalisations: (1) In monohalogenated and mononitroanilines replacement of the amino-group by a nitro-group proceeds regularly and, usually, with almost theoretical yields; exceptions are *m*-nitro-aniline, which gives a poor yield of *m*-dinitrobenzene, and certain compounds of analogous structure. (2) The amino-group in a monohalogenated nitroaniline or in a dinitroaniline may be replaced by a nitro-group by passing through the diazo-compound only when the new nitro-group enters in such a position that its elimination and replacement by an amino-group by heating with alcoholic ammonia is possible; Fry's theory, according to which the eliminability of nitro-groups depends on their polarity, is discussed. (3) Halogen atoms introduced into the benzene nucleus exert comparatively little influence on these transformations, which, however, they may render impossible if they occupy the 2-, 4-, or 6-position with respect to the amino-group; in other cases, however, they facilitate the changes or render them practicable to some degree. (4) It has not yet been found possible to introduce a new nitro-group into trinitro-substituted amines by diazotisation. (5) During the substitution of the amino-group by the nitro-group, certain aromatic amines, especially those containing no strongly electro-negative substituent elements or groups in the nucleus, are converted into the corresponding mononitrophenols. T. H. P.

**Liquid Crystals of Anisylidene-*p*-aminoazotoluene. P.**  
GAUBERT (*Compt. rend.*, 1923, 176, 907—909).—Polemical. The author maintains the accuracy of his observations on the isotropic forms of anisylidene-*p*-aminoazotoluene, which have been disputed by Friedel (*this vol.*, ii, 223). G. F. M.

**Existence of an Unidentified Sulphur Grouping in the Protein Molecule. I. On the Denaturation of Proteins.** LESLIE J. HARRIS (*Proc. Roy. Soc.*, 1923, [B], 94, 426-441).—It has been found that, whereas crystalline egg-albumin does not give the sodium nitroprusside reaction, a strongly positive reaction is given with the denatured protein. It is suggested that the denaturation of proteins involves the setting free of a reactive group, probably sulphydrol. It is considered probable that in heat coagulation of proteins a chemical change into metaprotein first takes place, followed by a physical change into the coagulated protein.

W. O. K.

**Existence of an Unidentified Sulphur Grouping in the Protein Molecule. II. On the Estimation of Cystine in certain Proteins.** LESLIE J. HARRIS (*Proc. Roy. Soc.*, 1923, [B], 94, 441-450).—Cystine is estimated by hydrolysis of the protein and isolation of the cystine under standard conditions. The actual amount found is estimated multiplied by 100/39.53, this factor being based on the amount of cystine isolated after hydrolysis, from gelatin to which a definite amount of pure cystine had been added. Whereas, in serum-albumin, the cystine accounts for no less than 89% of the total sulphur content, in ovalbumin 86% of the sulphur still remains to be accounted for.

W. O. K.

**The Action of Sodium Chloride on Collargol.** A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1848-1851).—It is shown that if a collargol solution is coagulated by acetic acid, and a sodium chloride solution slowly added, the coagulated silver at first redissolves and then, as the concentration of sodium chloride increases, is reprecipitated. This phenomenon is explained by the adsorption law, according to which adsorption is a function of ionic concentration. It is assumed that at low concentrations, chloridion is more adsorbed than natrion, whilst at higher concentrations the reverse is the case. Thus, in the former case, a preponderating quantity of negatively charged chloridions is adsorbed by the discharged particles of silver, which thus acquire a negative charge, and once again go into solution. When, however, the concentration of sodium chloride rises beyond a certain point, more natrions are adsorbed on the particles than chloridions, and their negative charge is again neutralised, causing them to be reprecipitated.

R. T.

**Autoclave Hydrolysis of Proteins with Carbon Dioxide and Oxalic Acid.** V. S. SADIKOV (*Biochem. Z.*, 1923, 136, 238-240).—Egg-albumin and goose feathers were hydrolysed by aqueous solutions of carbon dioxide under pressure in an autoclave at 160-185°. The biuret reaction was negative. Gelatin and casein under similar conditions with oxalic acid gave products soluble in alcohol which do not give the biuret or ninhydrin reaction. The results are preliminary.

H. K.

**Products of the Catalytic Fission of Proteins.** V. S. SADIKOV and N. D. ZELINSKY (*Biochem. Z.*, 1923, 136, 241-249).—This

aper is a description of results obtained for which the experimental details and methods of separation are promised later. ix kg. of goose feathers were hydrolysed in an autoclave at 180° with 1% hydrochloric acid for six hours. The product does not give the biuret reaction. It was extracted successively with ether, ethyl acetate, chloroform, and amyl alcohol, which accounted for 90% of the material. The ethereal extract contained crystalline anhydrides, a number of which have been identified, and a syrupy mixture of anhydrides. The ethyl acetate contained crystalline and syrupy anhydrides and free amino-acids. The chloroform extract contained syrupy and crystalline anhydrides. The amyl-alcoholic extract contained anhydrides and free amino-acids. The aqueous liquor left after extraction with solvents contains simple and complex amino-acids and also nitrogen-free acids. H. K.

**Determination of the Rate of Digestion of Albumin.** A. FRIEDERICH (*Chem. Ztg.*, 1923, 47, 265—266).—The increase of concentration of soluble albumin taking place during the process of digestion with pepsin is measured by means of Löwe's interferometer (*ibid.*, 1921, 45, 405, 1025), which admits of a high degree of accuracy. 2.5 Grams of the substance under examination are placed in a 250 c.c. flask together with 150—200 c.c. of water and 10 c.c. of dilute hydrochloric acid. The mixture is incubated at 37° and repeatedly shaken until the interferometer readings of two samples filtered off at intervals of one hour are the same, showing that all soluble albumin has gone into solution. 0.5 Gram of pepsin is then added and the volume in the flask made up to the mark with water at 37°. The contents are shaken and 1 c.c. is filtered off and its interferometer reading taken as the zero reading of the solution. The contents of the flask are incubated at 37° and small samples withdrawn and filtered every hour and their interferometer readings taken until these readings remain constant. A larger quantity of the solution is then filtered and the soluble albumin in the clear filtrate estimated by a micro-Kjeldahl method. This gives the total digestible albumin present, and enables the interferometer readings to be transposed into terms of percentage of albumin digested. The method gives consistent results. The data from two specimen analyses and curves showing the rate of digestion in each case are given. One sample was completely digested in two hours, whilst the other required twenty-seven hours. The percentages of digestible albumin present were 82.6 and 67.6, respectively. Other methods only showed a trifling difference between these two samples. H. C. R.

**Conphaseolin. A New Globulin from the Navy Bean, *Phaseolus vulgaris*.** HENRY C. WATERMAN, CARL O. JOHNS, and D. BREESE JONES [with S. PHILLIPS] (*J. Biol. Chem.*, 1923, 55, 93—104).—In addition to the globulins phaseolin and phaselin isolated by Osborne (A., 1896, i, 454; 1897, i, 207), the navy bean contains a third globulin, *conphaseolin*. This has been isolated by fractional precipitation of a sodium chloride extract of the bean with ammonium sulphate. Conphaseolin resembles the  $\alpha$ -globulins

obtained from other beans of the genus *Phaseolus* (cf. for example, A., 1922, i, 1101), and is distinguished from phaseolin and phaseclin by its high sulphur content. Analysis by Van Slyke's method gave the following values for basic amino-acids: Cystine 1.18%, arginine 6.87%, histidine 0.85%, lysine 10.69%. Phaseclin has been similarly analysed, with the following results (cf. A., 1920, i, 401): cystine 1.16%, arginine 6.36%, histidine 2.36%, lysine 9.42%.

E. S.

**Chlorinated Proteins.** E. SALKOWSKI (*Biochem. Z.*, 1923, 136, 169—189).—Albumose and casein have been chlorinated. Chloro-casein on hydrolysis yields the same products as casein with fewer reducing substances. It is very resistant to pepsin and trypsin, and shows little tendency to putrefy.

H. K.

**The Optical Properties of Leguminates of the Alkali Metals.** M. A. RAKUZIN and G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1888—1889).—Various optically active alkali metal leguminates have been prepared, and their optical rotations measured: the ammonium salt has  $[\alpha]_D -67.33^\circ$ , the lithium salt,  $[\alpha]_D -38.66^\circ$ , the sodium salt,  $[\alpha]_D -39.31^\circ$ , and the potassium salt,  $[\alpha]_D -39.62^\circ$ . The low values obtained for the last three salts are undoubtedly due to racemisation, but a gradual increase in the optical rotation is observable with increasing atomic weight of the metal. R. T.

**Crystals of Hæmoglobin of Rodents, particularly of the Hamster (German Marmot).** OTTO KRUMMACHER (*Z. Biol.*, 1923, 77, 175—180).—Crystals of hæmoglobin prepared from the blood of a hamster have been found to belong to the monoclinic system. Those obtained from most other mammals are rhombic, except those from the squirrel, which are hexagonal. Those from the pigeon are quadratic.

W. O. K.

**The Effect of Carbon Dioxide and Acetic Acid on the Osmotic Pressure of Hæmoglobin.** HELENE CONNET WILSON (*Biochem. J.*, 1923, 17, 59—71).—The osmotic pressure of solutions of purified hæmoglobin is three or four times as great when dialysed against acetic acid or water saturated with carbon dioxide (both about  $P_H 4$ ) as against water alone. The author is of the opinion that this phenomenon is due to the ionisation of some salt of hæmoglobin such as the one which ionises into protein-ions, or into protein- and acetate-, or protein- and bicarbonate-ions.

S. S. Z.

**Preparation and Estimation of Guanylic Acid: the Solubility of Sodium Guanylate in Salt Solutions and Water.** R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1923, 125, 284—288).—The solubility of sodium guanylate in solutions of sodium acetate and of sodium chloride has been determined, with reference to the isolation of guanylic acid as the sodium salt by Feulgen's method, which depends on the relative insolubility of that acid in sodium acetate solution (A., 1921, i, 136). W. O. K.

**Keratin. III.** A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1923, 126, 130—142; cf. this vol., i, 69).—By the use of

the iron method of Siegfried, a peptone has been isolated from the products of the partial hydrolysis of horn (cf. *loc. cit.*), having the empirical formula  $C_{11}H_{20}O_5N_3$  and  $[\alpha]_D^{20} -15.5^\circ$  approx.

W. O. K.

**A New Synthesis of *r*-Tryptophan.** RIKO MAJIMA and MUNIO KOTAKE (*J. Chem. Soc. Japan*, 1922, 43, 926–936).—*r*-Tryptophan has been synthesised from indole. Alessandri (A., 1915, i, 988) failed to obtain  $\beta$ -indolealdehyde,  $C_8H_7N\cdot CHO$ , from magnesium indole halide and formic ester using ether as a solvent, whilst the authors have succeeded in obtaining the aldehyde by the same method using anisole as a solvent, the yield being 40%. When phenetole was used instead of anisole, the yield decreased to about 23%, and when ethyl ether, amyl ether, or dimethylaniline were used, the aldehyde was not obtained. Using ethoxymethyleneaniline instead of formic ester, the aldehyde was also obtained, but the yield was less and the product was impure.  $\beta$ -Indolehydanitoin,  $C_8H_7N\cdot CH\cdot C_3H_2O_2N_2$ , is formed by heating  $\beta$ -indolealdehyde and hydanitoin with anhydrous sodium acetate and acetic anhydride at  $106$ – $108^\circ$  during thirty minutes; the product was boiled with alcohol and filtered after cooling and the residue dissolved into *N*-sodium hydroxide solution, precipitated by acidifying the solution with acetic acid, and crystallised from glacial acetic acid, the yield being 46.6%.  $\beta$ -Indolehydanitoin is reduced by sodium amalgam in sodium hydroxide solution to *o*-hydanitoylskatole,  $C_8H_7N\cdot CH_2\cdot C_3H_3O_2N_2$  (yield 68%), which is then decomposed into *r*-tryptophan,  $C_8H_7N\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$ , by heating with saturated baryta water at  $108^\circ$  for six hours, the yield being 53%. The product forms long, hexagonal plates with silky lustre, and decomposes at  $283$ – $285^\circ$ . As a by-product, an unknown compound,  $C_{12}H_{13}O_3N_3$ , crystallising in plates, m. p.  $207^\circ$  (decomp.), is obtained.

K. K.

**Apparatus for Preparing Dry Powders of Dissolved or Suspended Thermolabile Substances.** DAG SALOMONSON and H. VON EULER (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 24, 1–3).—The loss of activity of enzyme solutions by alcohol precipitation may be diminished by concentrating at low temperatures and pressures before precipitating. Dry preparations of enzymes are readily obtained by using a modified form of Krause's apparatus (D.R.P. 297388 of 1918). The solution or suspension to be evaporated is blown by means of carbon dioxide from a capillary jet surrounded by a slightly wider one through which the same gas is blown, warm carbon dioxide ( $70^\circ$ ) being blown through a third jet enclosing the other two. The jets pass into a large glass cylinder, the other end of which is covered with silk. The dry material collects in the cylinder. Air may be used for evaporating yeast solutions by this method, but for enzymes carbon dioxide is essential, to prevent oxidation.

E. E. T.

**Nomenclature of Proteases.** CARL OPPENHEIMER (*Biochem. Z.*, 1923, 136, 140–141).—The proteases can be provisionally

classified as follows. A. *True proteases* which break down protein to the peptide stage. These include *pepsinases*, characterised by an optimum in acid solution, *trypsinases* with an optimum zone near neutrality. B. *Peptidases* or *creptases* which only split peptides or peptones.

H. K.

**Saccharase.** H. VON EULER and KARL JOSEPHSON (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 23, 1-9).—The amino-nitrogen present in saccharase has been estimated by Van Slyke's methods (A., 1916, ii, 61). About two-thirds of the total nitrogen present is apparently in ring-combination. The following figures are given for the complete analysis of saccharase: ash 1-4, phosphorus 1-2, hexoses 60-20, pentoses under 5, total nitrogen 5-8, amino-nitrogen 2, easily-eliminable nitrogen about 1 per cent. These figures do not seem to be at variance with the suggestion that saccharase contains nucleic acid groupings (cf. A., 1922, i, 959), although the absence of positive tests for pentoses makes it improbable that Levene's type of nucleotide groupings is present. It is thought that combination between saccharase and sucrose is more likely to be due to partial valency addition than to adsorption.

The irreversible inactivation of saccharase by iodine (cf. A., 1922, i, 1076) has been further studied. It is now found that saccharase, cinnamic acid, benzaldehyde, and alanine behave similarly in not combining with or adsorbing iodine in dilute aqueous solutions. Bromine, under similar conditions, is taken up by saccharase, 1 g. of which combines with or adsorbs 0.48 g. of bromine. Cinnamic acid combines with 1 molecular proportion of bromine in like circumstances, alanine reacts with bromine in amounts depending on time, whilst benzaldehyde scarcely reacts at all. The authors therefore refrain from discussing the presence of definite groupings in the saccharase molecule.

E. E. T.

**Inactivation of Saccharase by *p*-Phenylenediamine, *p*-Toluidine, and Formaldehyde.** H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1923, 125, 297-314).—*p*-Phenylenediamine and *p*-toluidine inhibit the action of saccharase (invertase), the former being the more effective if they are applied in molecular proportions. The action of *p*-phenylenediamine decreases with increase in the concentration of the substrate and is minimal at a  $P_H$  of about 3.5. Similar effects are obtained with *p*-toluidine, the exact effect of the hydrogen-ion concentration depending on the amount of the inhibitor added. Preliminary incubation of enzyme and inhibitor before addition of sugar appears to have little effect, whereas the inhibiting effect of formaldehyde is increased by such incubation. Diphenylphosphoric acid also inhibits the action of invertase, an effect which decreases with increasing acidity.

W. O. K.

**Purification of Yeast-saccharase.** KARL JOSEPHSON (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 26, 1-21).—An examination of the methods used by Willstätter and Racke (A., 1922, i, 598) for the

preparation of saccharase. It is found that bottom-yeast is better for this purpose than top-yeast, presumably because it is freer from yeast-gum. Purification is effected by the following series of processes: autolysis in presence of 10% of toluene and 1% of ethyl acetate; filtration; precipitation with alcohol; dissolution in water and adsorption on aluminium hydroxide, using as small a volume as possible; elution, using potassium dihydrogen phosphate and sucrose solution; and dialysis through collodion membranes (Euler and Svanberg, A., 1920, i, 689). Kaolin then removes yeast-gum, by adsorption, as stated by Willstätter and Racke, and affords very active saccharase. A second adsorption on aluminium hydroxide, followed by elution, gives a still more active product, whereas a second kaolin adsorption effects no improvement. Adsorption on cupric hydroxide apparently causes complete loss of activity, whilst sugar-charcoal adsorbs neither saccharase nor the accompanying substances. For further work, see Euler and Josephson (this vol., i, 402).  
E. E. T.

### Poisoning of Starch Amylase; Starch Liquefaction. III.

URBAN OLSSON (*Z. physiol. Chem.*, 1923, 126, 29—99).—A comparison of the effect of copper sulphate, iodine, and aniline on the liquefaction of starch and on the production of sugar from it by malt diastase shows that the decrease in activity in the first two cases is quantitatively parallel, whilst in the case of aniline the liquefactive power is practically unaffected, although the sugar-producing power is decreased up to 21%. The method previously described (A., 1922, ii, 401) is adapted to quantitative measurement of the liquefactive power. It is found that the amount of sugar corresponds with a unimolecular reaction, whilst the liquefactive power is proportional to the amount of enzyme.

The effect of silver nitrate on maltase is proportional to the amount of the salt present, except with comparatively large amounts, when the decrease in activity lessens in proportion to the amount of silver nitrate present.  
W. O. K.

### The Reversibility of the Ferment Action of $\alpha$ -*D*-Mannosidase.

H. HÉRISSEY (*Compt. rend.*, 1923, 176, 779—782).—The action of  $\alpha$ -*D*-mannosidase is reversible, and according to the composition of the medium in which it is working it can bring about either the hydrolysis of a *D*-mannoside to mannose, or the synthesis of the mannoside from mannose. In a medium consisting of 10% methyl alcohol and about 1% of either mannose or  $\alpha$ -*D*-methylmannoside, in identical position of equilibrium is eventually reached in each case which corresponds with 46—47% of the methylmannoside.

G. F. M.

**Urease. I. The Chemical Changes Involved in the Zymolysis of Urea.** WILLIAM ROBERT FEARON (*Biochem. J.*, 1923, 17, 84—93).—Cyanic acid has been isolated as the silver salt from solutions of urea undergoing decomposition by urease. It is suggested that urease acts as a dissociating enzyme which decomposes the neutral urea molecule into ammonia and cyanio

acid; the latter is further decomposed by the solvent into ammonia and carbon dioxide. The cyanic acid attains a maximum concentration in the urea-urease system and is being produced as fast as it is hydrolysed. The decomposition of urea through the medium of the enzyme proceeds similarly to the normal decomposition of urea by acids, alkalis, and heat.

S. S. Z.

**Vitamins.** H. VON EULER and ALLAN BERNTON (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 21, 1—9).—Continuing previous work (A., 1908, ii, 724), the authors have isolated from carrots a *phosphatide*,  $C_{48}H_{88}O_{13}N$  (or  $N_2$ )P, and a *sterol*,  $C_{25}H_{44}O$ , m. p. 142°. The latter substance causes no appreciable increase in the fermentation of dextrose by bottom-yeast (freed from co-enzyme by previous washing and drying) in presence of sodium phosphate at  $p_H$  4.5. The fermentation of dextrose by a similar yeast is unaffected by sodium pyruvate in presence of sodium phosphate at  $p_H$  5 (cf. Neuberg, A., 1915, i, 1045).

E. E. T.

**Additive Reactions of Phosphorus Halides. VII. Addition of Alkyl- and Aryl-alkoxy-chlorophosphines to Carbonyl Compounds.** J. B. CONANT, V. H. WALLINGFORD, and S. S. GANDHEKER (*J. Amer. Chem. Soc.*, 1923, 45, 762—768).—A continuation of previous work (A., 1918, i, 74; 1920, i, 454; 1921, i, 69; 1923, i, 69, 186) dealing with the 1:2 and 1:4 addition of phosphorus trichloride and its aryl derivatives.

Benzaldehyde condenses at the ordinary temperature, in the presence of acetic acid, with phenoxydichlorophosphine, methoxydichlorophosphine, and ethoxydichlorophosphine, forming, respectively, the *phenyl*, *methyl*, and *ethyl* esters of  $\alpha$ -hydroxybenzylphosphinic acid,  $OH\cdot CHPh\cdot PO(OH)\cdot OR$ , as oils; the constitution of these esters is proved by the production of  $\alpha$ -hydroxybenzylphosphinic acid on hydrolysis by means of 15% aqueous hydrochloric acid, the free acid being readily identified as its aniline salt.

Phenoxydichlorophosphine condenses with phenyl styryl ketone in the presence of acetic acid, or, better, acetic anhydride, with formation of phenyl  $\beta$ -benzoyl- $\alpha$ -phenylethylphosphinate.

In the presence of acetic acid, diphenoxychlorophosphine undergoes the following condensations: with benzaldehyde, to form *diphenyl  $\alpha$ -hydroxybenzylphosphinate*, m. p. 146°, identified by hydrolysis to the acid; with acetone, to form *diphenyl  $\alpha$ -hydroxyisopropylphosphinate*, m. p. 113—114°, *acetate*, m. p. 72—72.5°; with methyl ethyl ketone, to form *diphenyl  $\alpha$ -hydroxyisobutylphosphinate*, m. p. 128.5°; with acetophenone, to form *diphenyl  $\alpha$ -hydroxy- $\alpha$ -methylbenzylphosphinate*, white cubes, m. p. 143.5°. *Diphenyl  $\alpha$ -hydroxy- $\beta$ -chloroisopropylphosphinate*, white cubes, m. p. 119°, is formed from chloroacetone and diphenoxychlorophosphine in the presence of benzoic acid, but those substances do not condense in the presence of acetic acid.

The diphenoxychlorophosphine used in these experiments is prepared by heating phosphorus trichloride (0.5 mol.) with triphenylphosphite (1 mol.) for six hours at 150°; the yield is 90% of theory.

W. S. N.

**Organic Arsenic Derivatives.** HEINRICH WIELAND (*Annalen*, 923, 431, 30–40).—[With A. KULENKAMPFF.]—The direct introduction of arsenic into the benzene nucleus (cf. Michaelis and Tabinerson, A., 1892, 1321) is accomplished by the addition of aluminium chloride (2.5 mols.) to a boiling solution of arsenic trichloride (1 mol.) in a large excess of benzene. Since aromatic arsenic derivatives are decomposed by aluminium chloride, 30–0% of the total arsenic present is converted into the free element; the remainder appears as phenylarsine dichloride (5 parts), diphenylarsine chloride (1 part), and triphenylarsine (14 parts). [With W. LADELUNG.]—Triphenylarsine is also obtained in 60% yield by the gradual addition of diphenylarsinic acid (26 g.) to warm phenylhydrazine (11 g.); the suggested mechanism of this reaction is indicated by the following equations: (1)  $\text{AsPh}_2\text{O}\cdot\text{OH} + \text{NH}_2\cdot\text{NHPh} = \text{AsPh}_2\cdot\text{OH} + \text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_2\text{O}$ . (2)  $\text{AsPh}_2\cdot\text{OH} + \text{NH}_2\cdot\text{NHPh} = \text{AsPh}_2\cdot\text{NH}\cdot\text{NHPh} + \text{H}_2\text{O}$ . (3)  $\text{AsPh}_2\cdot\text{NH}\cdot\text{NHPh} + \text{AsPh}_2\text{O}\cdot\text{OH} = \text{AsPh}_2\cdot\text{N}\cdot\text{NPh} + \text{AsPh}_2\cdot\text{OH} + \text{H}_2\text{O}$ . (4)  $\text{AsPh}_2\cdot\text{N}\cdot\text{NPh} = \text{Ph}_3\text{As} + \text{N}_2$ . If phenylarsinic acid is used, the reaction proceeds less readily, whilst arsenic acid is merely reduced to arsenious acid.

[With A. BLOEMER.]—When acetylene is led into a cooled mixture of aluminium chloride and arsenic trichloride, addition of the latter to the triple bond of the acetylene occurs (cf. A., 1922, i, 1033), with formation of *β-chlorovinylarsine dichloride*, a colourless oil, b. p. 7–78°/12 mm., which reacts with a second molecule of acetylene to give *di-β-chlorovinylarsine chloride*, a heavy, colourless oil, b. p. 13°/11 mm., previously described by Dufert (*Monatsh.*, 1919, 40, 13) as a molecular compound. This secondary arsine chloride combines with a further molecule of acetylene, forming *tri-β-chlorovinylarsine*, a colourless oil, b. p. 138°/12 mm., m. p. 13°. All three compounds appear in the product. The tertiary arsine is apparently not attacked by dilute hydrogen peroxide, but the secondary and primary arsine chlorides are readily oxidised to *di-β-chlorovinylarsinic acid*, long, glistening prisms, m. p. 122°, and *β-chlorovinylarsinic acid*, long, glistening plates, m. p. 129°, respectively, both of which are decomposed by concentrated alkali hydroxide into acetylene, hydrogen chloride, and arsenic acid.

[With H. WESCHE.]—*Cacodyl carbide*, a golden-yellow oil, b. p. 45°/14 mm., has been prepared by the gradual addition of cacodyl chloride to a suspension of magnesium acetylene bromide in boiling ether; the substance is highly unsaturated, explodes in contact with nitric acid, and is reconverted by alkali into acetylene, with elimination of the arsine radicle. W. S. N.

**Arsenated Benzanilide and its Derivatives.** W. LEE LEWIS and C. S. HAMILTON (*J. Amer. Chem. Soc.*, 1923, 45, 757–762).—The arsenated benzanilides are prepared by the action of *p*-dichloroarsinbenzoyl chloride (1 mol.) on aromatic amines in benzene solution. The impure product, which still contains chlorine united to the arsenic, is isolated as the arsenic acid after oxidation in glacial acetic acid solution by means of 3% hydrogen peroxide solution. The addition of sodium halide to the acetic acid solution gives the

corresponding dihalide, whilst the arsino-derivatives are best prepared by reduction by means of phosphorous acid or hypophosphorous acid in hot concentrated alcoholic solution.

The following arsino-compounds,  $\text{AsO}_3\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHR}$ , form colourless crystals of high melting point: *p*-Arsinobenzanilide, *p*-arsinobenzanthranilide, *p*-arsinobenzo-*p*-anisidide, *p*-arsinobenzo-*p*-phenetidide, and *p*-arsinobenzo-*o*-anisidide. *p*-Arsinobenzoyl-arsanilide,  $\text{AsO}_3\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ , is formed by the oxidation, by means of alkaline hydrogen peroxide, of hydrated *p*-arsinosobenzoylarsanilide,  $\text{As}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ , produced by the condensation of arsanilic acid with *p*-dichloroarsinebenzoyl chloride. The following arseno-compounds,  $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHR})_2$ ,

are yellow, insoluble, and of high melting point. *p*-Arsenobenzanilide, *p*-arsenobenzanthranilide, *p*-arsenobenzo-*p*-anisidide, *p*-arsenobenzo-*p*-phenetidide, *p*-arsenobenzo-*p*-xylylidide, *p*-arsenobenzo- $\alpha$ -naphthylidide. The following halogen derivatives are described: *p*-di-iodoarsinebenzo-*p*-anisidide, yellow needles, m. p. 209—210°, *p*-di-iodoarsinebenzo-*p*-phenetidide, yellow needles, m. p. 227—228°; *p*-di-iodoarsinebenzethylanilide, canary-yellow needles, m. p. 115—116°, *p*-di-iodoarsinebenzo-*o*-anisidide, m. p. 148—149°, *p*-dibromoarsinebenzo-*o*-anisidide, slightly yellow crystals, m. p. 167—168°, *p*-dichloroarsinebenzo-*o*-anisidide, slightly yellow crystals, m. p. 164—165°, *p*-dichloroarsinebenzethylanilide, colourless cubes, m. p. 147—148°.

Gluconic acid condenses rapidly with *p*-arsanilic acid in hot methyl-alcoholic solution to form *gluconyl-p*-arsanilic acid,  $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ , and more slowly in cold methyl-alcoholic solution with 3:4-diaminophenylarsinic acid to form 3:4-di(gluconylamino)phenylarsinic acid, yield 70%; both these acids are readily hydrolysed by means of dilute alkali.

W. S. N.

**Arsination of *o*-Cresol and *m*-Cresol.** WALTER G. CHRISTENSEN (*J. Amer. Chem. Soc.*, 1923, 45, 800—804).—In the arsination of *o*-cresol the formation of tar is much greater, the yield less, and the isolation of the products more difficult than in the case of phenol (Jacobs and Heidelberger, A., 1919, i, 604); the arsination of *m*-cresol proceeds with less formation of tar.

The action of arsenic acid on *o*-cresol at 155—160° leads to 6-hydroxy-*m*-tolylarsinic acid, 6:6'-dihydroxydi-*m*-tolylarsinic acid, 2-hydroxy-*m*-tolylarsinic acid, m. p. 198—200°, and 2:6'-dihydroxydi-*m*-tolylarsinic acid, m. p. 208—210°; the last two acids give a purple coloration with ferric chloride.

The action of arsenic acid on *m*-cresol at 140—146° leads to 5-hydroxy-*o*-tolylarsinic acid, 3-hydroxy-*o*-tolylarsinic or 3-hydroxy-*p*-tolylarsinic acid, m. p. 165—167°, giving a red coloration with ferric chloride. Secondary arsinic acids are also produced, which are not, however, completely separable, although a partial separation is effected by fractional decomposition of the calcium salts.

W. S. N.

**Preparation of *p*-Tolyl Mercury Compounds.** FRANK C. WHITMORE, FRANCES H. HAMILTON, and NEAL THURMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1066—1068).—The preparation of sodium toluene-*p*-sulphinat from toluene-*p*-sulphonyl chloride and zinc dust in aqueous suspension is described in an improved form, the yield being 80—90%. Sodium toluene-*p*-sulphinat and mercuric chloride react in boiling aqueous solution to give mercury *p*-tolyl chloride, yield 58%, which is converted into mercury di-*p*-tolyl by means of sodium iodide in boiling alcoholic solution, yield 80% (cf. Kharasch and Chalkley, A., 1921, i, 377). W. S. N.

**Reactions of Organic Mercury Compounds with Halides.**  
**I. Mercury Di-*p*-tolyl and Sulphonyl Halides.** FRANK C. WHITMORE and NEAL THURMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1068—1071; cf. preceding abstract).—Toluene-*p*-sulphonyl iodide reacts with mercury di-*p*-tolyl, in boiling carbon tetrachloride solution, to give di-*p*-tolylsulphone, mercuric iodide, and tolyl-mercuric iodide; toluene-*p*-sulphonyl chloride does not react under the same conditions, but this chloride or benzenesulphonyl chloride reacts with mercury di-*p*-tolyl at higher temperatures in toluene or xylene solution, giving, however, only traces of definite organic products. No mercury phenyl chloride is obtained by the action of benzenesulphonyl chloride on mercury di-*p*-tolyl. W. S. N.

## Physiological Chemistry.

**The Anticatalytic Action of Hydrocyanic Acid.** OTTO WARBURG (*Biochem. Z.*, 1923, 136, 266—277).—In opposition to Wieland's theory of cell respiration, but in support of the author's theory that cell respiration is catalysed by a surface effect of the heavy metals contained in living cells, experiments are detailed. Hydrocyanic acid in minute amounts inhibits the oxidation of leucine and oxalic acid by blood charcoal, but if the charcoal be heated with concentrated hydrochloric acid to diminish its content of iron, it still oxidises leucine and oxalic acid, but hydrocyanic acid has less inhibiting action. Hydrocyanic acid inhibits by attachment to the heavy metals and prevents the activation of oxygen. H. K.

**Observations on the Effect of High Altitude on the Physiological Processes of the Human Body, Carried Out in the Peruvian Andes.** JOSEPH BARCROFT and OTHERS (*Phil. Trans.*, 1923, [B], 211, 351—480).—The chief result obtained by the expedition is that the lungs do not secrete oxygen. The pressure of oxygen in the blood was so nearly the same as that in the alveolar air that the passage of the gas through the pulmonary epithelium can only be attributed to diffusion. The increased concentration of corpuscles at high altitudes is not merely to transport a certain quantity of

oxygen; it also brings about an extra degree of buffering of the blood, allowing of a more alkaline corpuscle at a given carbon dioxide pressure of 25 mm., a higher dissociation curve, and therefore a corpuscle which is more acquisitive of oxygen in the lung.  
G. E.

**The Respiratory Exchange, Blood-reaction, and Level of Phosphoric Acid in the Blood During Mental Work.** HUGO WILHELM KNIPPING (*Z. Biol.*, 1922, 77, 165—174).—Mental work is accompanied by only small increases in heat production. Nevertheless, on the commencement of such work, there is an immediate rise in the respiratory quotient which then rapidly decreases to a value below that found at rest. From analyses of the phosphoric acid content of the blood before and during mental activity, it is concluded that this effect is due to the entrance of free phosphoric acid into the blood with the consequent liberation of carbon dioxide.  
E. S.

**The Immediate Effect of Heavy Exercise (Stair-running) on some Phases of Circulation and Respiration in Normal Individuals. I. Oxygen and Carbon Dioxide Content of Blood Drawn from the Cubital Vein Before and After Exercise.** CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1923, 55, 315—321).—Heavy exercise, in which the muscles of the arm were not used, produced, in sixteen out of seventeen cases investigated, a marked decrease in the oxygen content of blood taken from the cubital vein. In one case, no change was observed. Variations in carbon dioxide were small and irregular. Possible explanations are discussed.  
E. S.

**The Inorganic Phosphorus Content of the Blood of Normal Children.** GRACE HAY ANDERSON (*Biochem. J.*, 1923, 17, 43—48).—The inorganic phosphorus content of the whole blood of twenty-four normal children between three months and thirteen years ranges from 4—6.6 mg. per 100 c.c. The average came to 4.9 mg. It is advisable to use whole blood for the estimation of phosphorus, as a considerable error may be obtained if serum is used which has been in contact with clot for some time. Twenty-four hours of fasting and a recent ingestion of a diet rich in phosphorus made no difference to the inorganic phosphorus content of the blood. The Bell-Doisy method for the estimation of phosphorus which was employed was found to have a range of experimental error of not more than plus or minus 10%.  
S. S. Z.

**The Calcium Content of the Blood during Pregnancy.** SYBIL TAITE WIDDOWS (*Biochem. J.*, 1923, 17, 34—40).—The calcium metabolism during pregnancy is so well balanced that the blood maintains a constant value in spite of varying demands made on it by the fetus during this period. Even in the later stages of pregnancy, when these demands are high, no diminution in the calcium content of the blood is observed.  
S. S. Z.

**Carbohydrate Metabolism. I. Some Comparisons of Blood-sugar Concentrations in Venous Blood and in Finger Blood. II. An Interpretation of the Blood-sugar Phenomena following the Ingestion of Dextrose.** G. L. FOSTER (*J. Biol. Chem.*, 1923, 55, 291—301, 303—314).—I. Preliminary experiments indicated that the sugar concentration of arterial blood is identical with that of blood drawn from the finger tip. Hence the latter was used in place of arterial blood for the purpose of comparing the concentrations of sugar in venous and arterial blood during periods of active sugar absorption. The results show that, in the fasting condition, the concentrations are identical. After ingestion of dextrose or starch, the initial rise in concentration is much greater in finger than in venous blood; the subsequent hypoglycæmia is, moreover, much less marked in the case of finger blood. Ingestion of levulose is followed by a slight rise in the sugar concentration of both finger and venous blood, that in the latter being sometimes practically absent; apparently levulose is much more completely absorbed by the liver than dextrose. No marked hypoglycæmia was observed in the case of levulose. Galactose causes a much higher level of hyperglycæmia than dextrose, the values for venous and finger blood being similar. This agrees with the fact that galactose is a poor glycogen former. Contrary to the results of Cammidge, Forsyth, and Howard (A., 1922, i, 81), the ingestion of a non-carbohydrate (agar-agar) meal produced no change in blood-sugar. II. Experiments are reported which support the conclusion of McLean and de Wesselow (*Quart. J. Med.*, 1921, 14, 103) that glycogen formation is stimulated by a rise in blood sugar, thus preventing excessive hyperglycæmia after the ingestion of dextrose. Further, the subsequent hypoglycæmia is due to over-activity of the glycogen-forming mechanism. E. S.

**Blood Gas Analysis. XIII. Influence of  $\alpha$ -Rays on Hæmoglobin and Blood-corpuscles. II.** STRAUB and KL. GOLLWITZER-MEIER (*Biochem. Z.*, 1923, 136, 128—139).—The action of positively charged  $\alpha$ -rays and of radium-*F* on hæmoglobin and suspensions of corpuscles in isotonic sodium chloride solution is to effect a change in the form of the curves obtained by plotting the carbon dioxide in combination against the tension. The results are held to support the authors' views on the existence of an electrical double layer at the boundary surface of corpuscles,  $\alpha$ -rays neutralising the negative charge. H. K.

**An Uneven Ionic Exchange between Corpuscles and Phosphate Buffer Mixtures of Increasing Hydrogen-ion Concentration.** CHRISTMAN KROETZ (*Biochem. Z.*, 1923, 136, 250—265).—When washed corpuscles were added to phosphate mixtures of known  $p_H$  and then centrifuged after fifteen minutes, the  $p_H$  redetermined colorimetrically was always more alkaline, and although the original phosphate mixtures made up were of increasing  $p_H$ , the redetermined values after treatment with corpuscles, although higher, showed a tendency to retain a constant

value. An analogy is drawn with the parallel results of the carbon dioxide combination curve of hæmoglobin of Straub and Meier.

H. K.

**Inorganic Phosphorus of the Serum and Plasma of Ninety-one Normal Adults as Determined by the Bell and Doisy Method.** EDWARD TOLSTOI (*J. Biol. Chem.*, 1923, 55, 157—160).—The values found lie between 2.5 and 3.3 mg. of phosphorus per 100 c.c. Practically identical values were obtained for plasma and serum, provided the latter was not left for too great a time in contact with the clot.

E. S.

**The Increase of Calcium-ions in Human Serum after Intravenous Injection of Calcium Salts.** ERNST SIEBURG and ADOLF KESSLER (*Arch. expl. Path. Pharm.*, 1923, 96, 180—192).—After the injection of aqueous solutions of various calcium salts (chloride, formate, propionate, lactate) in amounts sufficient to double the calcium content of the blood, the concentration of calcium-ions (as distinct from total calcium) in the serum returned to the normal within half an hour. The effect of calcium hypophosphite was of shorter duration, probably owing to its rapid oxidation to phosphate. Admixture of the salts with gum arabic or agar-agar increased the time by about 25%; gelatin, however, had no such effect. Separate experiments on rabbits indicate that the condition of lipæmia has no influence on the rate of disappearance of injected calcium-ions.

E. S.

**Comparative Content of Plasma and of Serum in Lipoids.** (MME) PAULETTE JUNG and RENÉ WOLFF (*Bull. Soc. Chim. biol.*, 1923, 5, 137—147).—The blood lipoids appear to pass into the serum on coagulation, as the content of the serum in them is greater than that of the plasma. This difference is less, and in fact sometimes does not exist, in blood taken from fasting animals, and in those not fasting the difference varies, to some extent depending on the food which is being digested.

W. O. K.

**Mode of Action of Formaldehyde with the Colloids of the Organism. II.** H. KÜRTEN (*Biochem. Z.*, 1923, 135, 536—545).—Further experiments in support of the view that formaldehyde alters the state of serum proteins by a reversal of the state of swelling. The viscosity of the globulin and albumin fractions of sera were determined and compared with the value after heating at 60° for two hours. These values were then compared with the viscosities obtained after treatment with dilute formaldehyde solution. In each case the heated serum showed a greater reactivity to formaldehyde than the unheated.

H. K.

**So-called Anti-enzymes.** EMIL ABDERHALDEN and ERNST WERTHEIMER (*Fermentforsch.*, 1922, 6, 286—301).—The authors have made experiments with rabbits to ascertain if intravenous injection of an enzyme solution results in the appearance in the blood-serum of a substance with anti-enzymic properties, the enzymes employed being: polypeptidase from yeast maceration

juice and from pancreas, diastase from liver, lipase from pancreas, and saccharase obtained from yeast by Euler's method. In all cases were negative results obtained (cf. Knaff-Lenz, A., 1922, i, 694). Even highly active saccharase preparations are incapable of undergoing dialysis.

T. H. P.

**Hæmolytic Experiments with Salts of the Alkalis and Alkaline-earths under Normal and Pathological Conditions.** KURT BECKMANN (*Biochem. Z.*, 1923, 135, 317—328).—Contrary to Hamburger's results, but in agreement with Höber's, the degree of hæmolysis of blood-corpuscles is not the same for isotonic solutions. Over the range of hæmolysis from 0 to 100%, the kations combined with chloridion produce hæmolysis in the following order of effectiveness:  $K > Rb > Li > Na > Cs$ ;  $Ca > Ba > Sr, Mg$ , and for the anions in combination with potassium

$I > SCN > Cl > Br > NO_3 > SO_4$ .

Under pathological conditions, the same sequence of ions holds good with slight variations.

H. K.

**Does Injection of Peptone to Prevent Clotting Interfere with the Gaseous Metabolism?** G. KELEMEN (*Biochem. Z.*, 1923, 136, 154—158).—In experiments on a dog which received an intravenous injection of a 5% solution of Witte peptone to prevent blood-clotting, the oxygen consumption was considerably reduced and in all cases the respiratory coefficient increased. The conclusion is drawn that peptone cannot be used in experiments on the gaseous metabolism.

H. K.

**Chemical Kinetics of the Digestion of Carbohydrates in the Duodenum of Mammals.** CARL BÖHNE (*Fermentforsch.*, 1922, 6, 200—229).—The principal co-enzymes of the diastase of the pancreas in the animal organism are phosphates, carbonates, and sodium chloride. In presence of potassium dihydrogen phosphate, 2% amylose solution having  $p_H$  4.6—5 is digested by the enzyme in one hundred minutes, whilst with disodium hydrogen phosphate and  $p_H$  8.4—9.1, twelve hours are required. The activity of the two phosphate-diastases increases as the hydrogen-ion concentration approaches the neutral point. When a mixture of the two phosphates is present and the value of  $p_H$  is 5.9—6.9, the digestion occupies eighty minutes. In presence of sodium hydrogen carbonate and with  $p_H$  8.3, digestion is complete in twelve hours, but the intensity of the action varies with the concentration of the salt; if the latter is partly saturated with carbon dioxide, so that  $p_H$  becomes 6.7, the time of digestion is reduced to eighty minutes.

These results, depending mainly on the concentration of the hydrogen-ions, undergo marked alteration if small proportions of sodium chloride are added to the digestion mixture. If the latter has an alkaline reaction, sodium chloride activates the digestion to such an extent that the duration may be shortened from twelve hours to sixty to seventy minutes. Similar accelerating effects are produced by sodium chloride when the digestion liquid has

an acid reaction due to the presence of a mixture of either potassium dihydrogen phosphate and disodium hydrogen phosphate or sodium hydrogen carbonate and carbon dioxide. No explanation is advanced of the observation that, with either of these mixtures as co-enzyme, the optimum reaction for pancreatic diastase is displaced by sodium chloride towards the neutral point.

Thus the anions of the diastase-salt complexes,  $\text{Cl}'$ ,  $\text{HCO}_3'$ ,  $\text{H}_2\text{PO}_4'$ , and  $\text{HPO}_4''$ , effect conversion of an inactive, resting enzyme into the active state, the course of the digestive process being governed mainly by the hydrogen-ion concentration and, to a less extent, by the concentration of the added salt.

The physiological consequences of these results are discussed.

T. H. P.

**Carbohydrate Metabolism in Avitaminosis. II. Glycogen.** J. A. COLLAZO (*Biochem. Z.*, 1923, **136**, 20—25).—Deficiency of vitamins *A*, *B*, and *C* leads to a hyperglycæmic state in doves, fowls, guinea-pigs, and dogs, in which there is also a disappearance of glycogen from the various depôts. Under parallel conditions, fasting animals with slight hyperglycæmia show a higher liver, heart, and muscle content of glycogen.

H. K.

**Carbohydrate Metabolism in Avitaminosis. III. Influence of Dextrose Administration.** J. A. COLLAZO (*Biochem. Z.*, 1923, **136**, 26—37).—The author has examined the effect on the blood-sugar of the oral, rectal, intraperitoneal, intravenous, and subcutaneous administration of dextrose in large and small quantities to normal or fasting dogs or to dogs suffering from avitaminosis. Large doses (80 g.) in avitaminosis produce a more pronounced and protracted hyperglycæmia than in fasting or normal animals, whilst small doses (5 to 10 g.) produce in all cases a slight hyperglycæmia followed by a return to the normal level in normal and fasting dogs, but showing a transient hypoglycæmia in avitaminosis.

H. K.

**Carbohydrate Metabolism in Avitaminosis. IV.** J. A. COLLAZO (*Biochem. Z.*, 1923, **136**, 278—290).—Administration of carbohydrates to animals in a state of avitaminosis produces toxic symptoms. Dextrose, lævulose, and galactose are highly toxic, sucrose, lactose, and maltose less toxic, and starch least of all. If vitamins (yeast) be given at the first manifestations of toxic symptoms, these symptoms vanish and the hyperglycæmic condition of the blood subsides. Five g. of yeast were always found sufficient to counteract 10 g. of dextrose. It is concluded that vitamins are essential to the cells for the metabolism of carbohydrates.

H. K.

**The Action of Thyroxin and of Very Small Amounts of Iodine [Potassium Iodide] on the Metabolism.** FRITZ HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1923, **96**, 292—304).—The identity of the physiological effects (increased oxygen consumption and decrease in body-weight) produced by injections of thyroxin and by the administration of thyroid gland by the mouth, observed

by Kendall, has been confirmed for rats. The effect of a thyroid-gland diet on rats is decreased by injection of small amounts of potassium iodide and increased by larger amounts. That the result in the former case is not due to an inhibition of the function of the thyroid gland has been shown by experiments on thyroid-ectomised animals.

E. S.

**Proteolytic Enzymes of the Lymph Glands.** S. G. HEDIN (*Z. physiol. Chem.*, 1923, **125**, 289—296).—When lymph glands are treated with dilute acid and subsequently extracted with a solution of casein, two enzymes are obtained, one with an optimum reaction of  $p_H$  5.5, and an erepsin, with the optimum reaction  $p_H$  8. If the glands are further extracted with a solution of sodium chloride, another proteolytic enzyme is obtained, optimum  $p_H$  9—10.

W. O. K.

**Oil of the Liver of *Squalus acanthias* from Moroccan Waters.** SERGIO BERLINGOZZI and MARIA TOMASINI (*Ann. Chim. Appl.*, 1923, **7**, 29—33).—This oil, expressed from the liver of the young fish, closely resembles cod-liver oil in its physical and chemical constants, and is readily converted into a solid fat by hydrogenation [cf. *J.S.C.I.*, 1923, May].

T. H. P.

**Pancreatic Enzymes. III. Pancreas Amylase.** RICHARD WILLSTÄTTER, ERNST WALDSCHMIDT-LEITZ, and ALBERT R. F. HESSE (*Z. physiol. Chem.*, 1923, **126**, 143—168; cf. this vol., i, 403).—The action of amylase in the glycerol extract of dried pancreas is influenced by the presence of salts and by the hydrogen-ion concentration. The production of sugar from starch follows approximately a unimolecular reaction, and is proportional to the amount of enzyme present. On the basis of these findings, a method is devised for the estimation of amylase, the result being expressed in amylase units, an amylase unit being that amount for which, under given conditions, the constant of unimolecular reaction is 0.01. The amylase value of a preparation is the number of amylase units in 1 cg.

To isolate amylase from the crude extract of pancreas, the lipase is adsorbed on aluminium hydroxide, and then the trypsin is adsorbed by kaolin from a solution made slightly acid with acetic acid. The amylase is further purified by adsorption from 50% alcohol. The adsorbability of amylase decreases with increasing purity. An amylase preparation with an amylase value of at least 1205 has been obtained. The purified material showed no protein reactions, but still gave Molisch's reaction. W. O. K.

**Polypeptide-cleaving Enzyme System in Pancreas Press-juice. Action of Vegetable Mucus on Enzyme Extracts of the Pancreas.** A. FODOR (*Fermentforsch.*, 1922, **6**, 269—285; cf. A., 1920, i, 464; 1921, i, 701).—By the method used to separate phosphorus-containing proteins in the sol-forming condition from yeast extracts, it is possible to obtain from pressed or maceration juice of the pancreas a phosphorus-containing protein approaching closely in composition those of yeast, but showing greater variations

in nitrogen and phosphorus content; thus purer products are obtainable from yeast juices than from animal cells and tissues.

The condition of the colloids in the pancreatic maceration juice has been investigated ultramicroscopically and experiments have been made on the influence exerted by carrageen extract on the polypeptidolytic activity of the juice. The results obtained indicate that the protein is the principal carrier of the enzyme action, but that the lipoids of the pancreas cells favour the suspensibility and the distribution of the enzyme colloids over large surfaces in virtue of their power of retarding aggregation and molecular agglomeration. The possibility of a connexion between enzymic activity and phosphorus content is discussed.

T. H. P.

**Tethelin: a Growth-controlling Substance obtainable from the Anterior Lobe of the Pituitary Body.** THORBURN BRAILSFORD ROBERTSON (*Biochem. J.*, 1923, **17**, 77—82).—Polemical. The author asserts that Drummond and Cannan's repetition of his work (A., 1922, i, 491) was vitiated by a faulty method of preparation of tethelin and by not adopting the statistical method of comparing the growth of animals receiving this dietary principle with that of normal animals.

S. S. Z.

**Muscle Respiration and Sarcoplasma.** GUSTAV EMBDEN and HERMANN LANGE (*Z. physiol. Chem.*, 1923, **125**, 258—283).—The skeletal muscles of frogs, if immersed in isotonic sucrose solution after being in Ringer's solution, show marked increase in oxygen consumption and increased liberation of phosphoric acid. These increases are accompanied by marked swelling of the sarcoplasma, and are greatest at a certain optimum swelling.

W. O. K.

**The Selective Absorption of Potassium by Animal Cells. III. The Effect of Hydrogen-ion Concentration on the Retention of Potassium.** RALPH E. STANTON (*J. Gen. Physiol.*, 1923, **5**, 461—468).—By perfusing frog's muscles with potassium-free Ringer solution of  $P_H$  from 6.0 to 8.0, it is shown that within this range the hydrogen-ion concentration has little or no effect on the retention of potassium.

W. O. K.

**Cholesterol Content of Various Muscles of Rabbits.** GUSTAV EMBDEN and HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, **125**, 199—209).—The cholesterol content of various muscles in rabbits has been determined by heating the muscle with a 25% solution of potassium hydroxide, extracting with ether, evaporating the ethereal extract, and using an aliquot part of the chloroform extract for colorimetric estimation (heating with acetic anhydride and sulphuric acid). The white musculus biceps femoris contains about 0.04—0.06% of cholesterol, the red musculus semitendinosus, and the diaphragm 0.07—0.10%, whilst the heart contains 0.12—0.16%.

W. O. K.

**The Cholesterol Content of Various Muscles.** HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, **125**, 210—219).—The cholesterol content of the muscles of various animals has been

investigated. It is concluded that in general there is a very strong parallelism between cholesterol content and resistance to fatigue.

W. O. K.

**Chemical Differences between Skeletal Muscles of the Calf and the Ox.** KAZUO HOTTA (*Z. physiol. Chem.*, 1923, 125, 220—228).—Analyses have been made of the nitrogen, cholesterol, and phosphoric acid contents of the biceps of the calf and the ox. There is more cholesterol, and correspondingly more "rest"-phosphoric acid, in the muscle of the calf than of the ox.

W. O. K.

**The Interconversion of Creatine and Creatinine. IV. Origin of Creatinine in the Organism.** AMANDUS HAHN and GEORG MEYER (*Z. Biol.*, 1923, 78, 91—118; cf. this vol., ii, 195).—Quantitative experiments on the serum, blood, liver, and kidney of the ox and on the liver of the pig and dog show that during sterile autolysis at 38° there is no destruction either of creatine or of creatinine and no interconversion of these substances. Where occasionally an increased creatinine content was observed, it was shown to be due to the development of acidity, for, by the use of buffer mixtures of the same acidity and added creatine, a transformation into creatinine followed. Ferments for the interconversion of creatine and creatinine or their destruction are non-existent. Similar relations hold for creatinine and creatine in urine. When creatine is taken by mouth in solution by man, there is no increased creatinine output in the urine. Subcutaneous injections of creatine in the rabbit do not cause an increased creatinine excretion, and the whole of the creatine is excreted in twenty-four hours. The origin of creatinine in man is ascribed to transformation of the creatine of muscle brought about by the reaction of the tissue.

H. K.

**Pigment in Horse Hair.** KARL TUTSCHKU (*Biochem. Z.*, 1923, 135, 585—586).—The hair of various coloured horses after washing with water was covered with a mixture of 75% alcohol and ether (9 : 1) for ten weeks. The solvent acquired a yellowish-green colour and gave the colour reactions for lipochrome with sulphuric acid and with nitric acid. The crystals obtained on removal of the solvent gave the Liebermann cholesterol reaction. If the hair is first of all treated with potassium hydroxide and filtered, the filtrate is free from lipochrome, but the insoluble matter when extracted with the alcohol-ether mixture gives the lipochrome reaction.

H. K.

**Structural Colour in Feathers. I.** CLYDE W. MASON (*J. Physical Chem.*, 1923, 27, 201—251).—The colours of feathers have been investigated. It is shown that the non-iridescent blue of feathers is due to the scattering of blue light by very fine pores in the walls of the outer layer of cells of the barbs of the feathers. This is the blue described by Tyndall, which is commonly observed in turbid media. No blue pigments, and no other structural causes of blue colour, have been observed in non-iridescent feathers.

Green feathers are essentially the same as blue feathers, except that the blue cells are overlaid by a transparent, yellow layer.

J. F. S.

**Substances Extracted from *Eledone moschata*.** I. D. ACKERMANN, F. HOLTZ, and F. KUTSCHER (*Z. Biol.*, 1923, 77, 241—244).—Adenine and arginine have been isolated from the mussel, *Eledone moschata*.

W. O. K.

**Chemical Composition of Coral from the Tyrrhenum.** N. PASSERINI (*Gazzetta*, 1923, 53, i, 35—40).—The percentage composition of bright red coral (*d* 2.640) gathered in the Tyrrhenian Sea about 10 kilometres south of Leghorn and air-dried, is found to be: water, 0.600; organic matter, 2.545; calcium carbonate, 85.495; magnesium carbonate, 9.102; calcium sulphate, 1.230; other mineral constituents and loss, 1.028; manganese and iron, scarcely detectable traces. These results are compared with those of other investigators.

T. H. P.

**The Sterol Content of Cow's Milk.** FRANCIS WILLIAM FOX and JOHN ADDYMAN GARDNER (*Biochem. J.*, 1921, 17, 94—102).—Cholesterol is present in milk in the free state and in the form of esters. These compounds are found to be present in proportions of 0.351 g. to 100 g. of milk-fat—a figure which is in close agreement with those obtained by other workers. The output of cholesterol appears to follow approximately the output of fat. Although most of the cholesterol (free and ester) is present dissolved in the milk fat, some of it is also present in another form in the milk. The fraction which is precipitated from the unsaponifiable fraction of milk by digitonin consists entirely of cholesterol. The remaining portion of the unsaponifiable fraction consists of oils which are in part at least stable esters capable of withstanding saponification by alkali. The chemical behaviour of these oils is described.

S. S. Z.

**The Rate of Decline of Milk Secretion with the Advance of the Period of Lactation.** SAMUEL BRODY, ARTHUR C. RAGSDALE, and CHARLES W. TURNER (*J. Gen. Physiol.*, 1923, 5, 441—444).—The average daily production of milk varies with the month of lactation, and is found to be given by the formula  $M_t = M_0 e^{-kt}$ , where  $M_0$  and  $k$  vary with the breed of cows. This is the formula of a unimolecular chemical reaction, and the result is considered to confirm the view that milk secretion is limited by a chemical reaction.

W. O. K.

**Influence of the Acid and Base Content of the Food on the Composition of the Urine of Growing Dogs.** JONAS BORAK (*Biochem. Z.*, 1923, 135, 480—492).—From consecutive experiments on a single dog or parallel experiments on two dogs of a litter, it was found that feeding with foodstuffs of an acid character such as rye meal, rye bread, or tripe resulted in a greater increase of weight than feeding with foodstuffs of a basic character such as milk, potatoes, carrots, and soja beans. The difference is

attributed to retention of water by the dogs fed on an acid diet, as nitrogen estimations on the food and urine showed a greater nitrogen excretion on an acidic diet than on a basic one, although the volume of urine in the former case was less than in the latter.

H. K.

**Influence of the Composition of Food on the Calcium Output.** B. SJOLLEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 395—398).—The variation of the amount of calcium and phosphorus in the faeces of a rabbit fed on various foods to which various amounts (3—12%) of non-digestible ballast have been added (such as oat straw or sawdust which had been boiled with acid and alkali) has been determined. The experiments show that an increase of the amount of non-digestible matter in the food causes a greater loss of calcium via the intestinal canal. All the calcium present in the faeces is not necessarily derived directly from the food, a large portion of it may be supplied by the organism, from which it is concluded that calcium plays a rôle in the production of faeces. In view of this, it follows that only under certain conditions can an examination of the faeces show whether calcium occurs in an available form in the food or in any part of it. In animals which are yielding much milk, feeding with much ballast increases the danger of a negative calcium balance.

J. F. S.

**The Selective Action of the Kidney as Regards the Excretion of Inorganic Salts.** W. DENIS (*J. Biol. Chem.*, 1923, 55, 171—181).—Analyses of the blood of dogs following the administration by the intestine or intravenously of magnesium sulphate, sodium sulphate, magnesium chloride, sodium chloride, and sodium phosphate indicate that the kidney exercises a selective retention for the sulphate-ion.

E. S.

**Rate of Excretion of Urea. V. The Effect of Changes in Concentration of Urea in the Blood on the Rate of Excretion of Urea.** T. ADDIS and D. R. DRURY (*J. Biol. Chem.*, 1923, 55, 105—111; cf. A., 1916, i, 352, 864; 1917, i, 367).—Under special conditions, the chief of which is abstention from food, the rate of excretion of urea is directly proportional to its concentration in the blood (cf. also Austin, Stillman, and Van Slyke, A., 1921, i, 383).

E. S.

**Rate of Excretion of Urea. VI. The Effect of Very High Blood Urea Concentrations on the Rate of Excretion of Urea.** D. R. DRURY (*J. Biol. Chem.*, 1923, 55, 113—118).—Experiments on rabbits indicate that the relation between the rate of excretion of urea and its concentration in the blood (preceding abstract) holds even when the latter is increased by injection to more than 700 mg. per 100 c.c.

E. S.

**Constituents of the Urine Known as "Oxyproteic Acid."** E. FREUND and ANNA SITTENBERGER-KRAFT (*Biochem. Z.*, 1923, 136, 145—153).—The preparation of oxyproteic acid from the

urine of carcinomatous patients is described and depends on the removal of foreign substances by alkaline copper sulphate and precipitation of the required acid by mercuric acetate. The amorphous barium salt precipitated by alcohol corresponds with an acid,  $C_{10}H_{22}O_{10}N_2$ . It had no characteristic protein reactions, but is possibly a derivative of carbamide, which it yields on hydrolysis.

H. K.

### Hydrogen-ion Concentration of the Blood in Carcinoma. I. From the Colorimetric Estimation of the Blood Dialysate.

WILLIAM H. CHAMBERS (*J. Biol. Chem.*, 1923, **55**, 229—255).—Estimations were made of the hydrogen-ion concentration of the dialysates from the venous blood of normal subjects and of patients suffering from carcinoma and other diseases. The method employed was similar to that of Dale and Evans (*A.*, 1921, i, 142); loss of carbon dioxide was prevented by carrying out the various stages under a layer of oil. The following are the average  $P_H$  values found at 20°: normal subjects 7.31, carcinoma cases 7.45, pathological cases other than carcinoma 7.36. The dialysates from the carcinoma patients were thus distinctly more alkaline than the others; the individual values show, further, that, in general, the alkalinity increased with the size of the tumour.

E. S.

### Hydrogen-ion Concentration of the Blood in Carcinoma. II. From the Carbon Dioxide-Bicarbonate Ratio.

WILLIAM H. CHAMBERS and R. E. KLEINSCHMIDT (*J. Biol. Chem.*, 1923, **55**, 257—290).—When calculated from the carbon dioxide-bicarbonate ratio, the hydrogen-ion concentration of the venous blood of carcinoma patients was found not to differ from that of normal subjects. The following are the average  $P_H$  values found at 38°: normal subjects 7.29, carcinoma cases 7.34, pathological cases other than carcinoma 7.33. The value found for normal blood at 38° thus agrees with that obtained from the dialysate at 20° (preceding abstract); at 38°, however, the latter would have a greater  $P_H$  value than the former. This greater alkalinity of the dialysate is explained by the authors on the basis of Donnan's theory of membrane equilibria. The same theory indicates that the still greater alkalinity of the dialysates from the blood of carcinoma patients is due to an increase of non-diffusible anions in the plasma.

E. S.

**Zinc in Cancerous Tissues. Physicopathology of Zinc, and, Particularly, its Significance in Tumours.** PAUL CRISTOL (*Bull. Soc. Chim. biol.*, 1923, **5**, 23—40).—Estimations have been made of the zinc present in the liver, spleen, and blood in a case of leucæmia, and in a large number of tumour tissues. The zinc content appears to vary with the activity of the tumour.

W. O. K.

**Behaviour of Cholesterol in Pigeon-Beri-beri.** HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, **125**, 229—247).—There is an increase of cholesterol in the skeletal muscles of pigeons suffering from avian beri-beri.

W. O. K.

**Influence of Cholesterol on the Consumption of Oxygen by Lecithin.** HERMANN LANGE and HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, 125, 248—257).—Ciaccio has shown that there is a diminution of lecithin, whilst Lawaczek (preceding abstract) shows there is an increase of cholesterol, in skeletal muscles in avian beri-beri. The antagonistic action of cholesterol and lecithin on intercellular respiration deduced from this is confirmed in the present research. The addition of cholesterol to an emulsion of lecithin containing ferric chloride influences the consumption of oxygen by the lecithin, a maximum being attained when a certain proportion of cholesterol to lecithin is present.

W. O. K.

**Change in the Nature of the Blood-sugar of Diabetics caused by Insulin.** W. DEVEREUX FORREST, W. SMITH, and L. B. WINTER (*J. Physiol.*, 1923, 57, 224—233).—The two last-named authors have recently shown (*J. Physiol.*, 1922, 57, 100) that the normal blood-sugar in man and in animals has a lower rotatory power than would be given by the  $\alpha$ - $\beta$ -equilibrium form of glucose as deduced from the copper reduction value. The sugar gives an osazone with the same crystalline form and melting point as that of glucosazone. The instability of the sugar is shown by its transient rotatory power, the curve of the polarimeter readings reaching the copper reduction value in three or four days in acid solution. The sugar at first decolorises potassium permanganate more rapidly than a solution of  $\alpha$ - $\beta$ -glucose in similar concentration. This distinction no longer obtains when the polarimeter reading corresponds with that of  $\alpha$ - $\beta$ -glucose. These facts, in conjunction with the work of Hewitt and Pryde (*A.*, 1920, i, 508, 648) on sugar solutions introduced into the intestine, suggest that normal blood-sugar is  $\gamma$ -glucose. In diabetes, it is shown that this sugar is not present in amounts capable of detection by the method employed. The polarimeter reading in this disease is initially greater than the copper reduction value, suggesting that, besides  $\alpha$ - $\beta$ -glucose, disaccharides or other substances with a higher polarimeter : copper reduction ratio are present in the blood of diabetic persons. It is suggested that  $\alpha$ - $\beta$ -glucose cannot be directly stored or utilised, but that an enzyme is responsible for the conversion of  $\alpha$ - $\beta$ -glucose into  $\gamma$ -glucose; the absence of this enzyme is suggested as the direct cause of diabetes mellitus.

In the present communication, the above observations are confirmed in seven cases. The greatest change in the rotation observed, due to the administration of insulin, was  $0.15^\circ$ , the smallest about  $0.01^\circ$  (cf. also *Annual Reports*, 1923, 49, 195).

G. B.

**An Enzyme Responsible for Alteration of the Rotatory Powers of Glucose and Fructose. Some Evidence for the Existence of Polysaccharides in the Blood of Diabetics. The Lowering of the Blood-sugar by an Extract of Yeast.** L. B. WINTER and W. SMITH (*Proc. Physiol. Soc.*, 1922, 1923; *J. Physiol.*, 1923, 57, xiii, xxxi, xl).—I. The enzyme appears to be present in the liver. Glucose and fructose solutions incubated

with very small amounts of insulin and liver extract have their rotations altered in a downward and upward direction, respectively. The insulin preparations are thermostable in this respect, and always contained phosphates; addition of phosphates accelerates the change in rotation. Boiled liver extracts are inactive.

II. Further evidence is obtained of the occurrence of polysaccharides (cf. preceding abstract).

III. A solid preparation of yeast has been obtained, which, like insulin, definitely lowers the blood-sugar on injection into rabbits. Rats, when it is injected, die in convulsions similar to those caused by insulin.

G. B.

**Influence of the Nutritional Condition of the Animal on the Hypoglycæmia Produced by Insulin.** N. A. McCORMICK, J. J. R. MACLEOD, E. C. NOBLE, and K. O'BRIEN (*J. Physiol.*, 1923, 57, 234—252; cf. *Annual Reports*, 1923, 19, 196).—The amount of glycogen in the animal has a distinct influence on the dose of insulin required to produce a given lowering of the blood-sugar, or to produce convulsions. Hence it is impossible to make a precise physiological assay of insulin by determining the percentage of blood-sugar at varying periods after the injection. An approximate assay can best be made by determining the blood-sugar ninety minutes, and three hours, after the injection in animals which have had no food for twenty-four hours.

G. B.

**Ammonia Content of the Blood in Nephritis.** DOROTHY STUART RUSSELL (*Biochem. J.*, 1923, 17, 72—76).—Estimations of blood-ammonia in a series of cases of advanced renal disease showed values under 0.1 mg.%. These values are of the same order as those found in the blood of normal patients. The author suggests that this observation lends support to Nash and Benedict's hypothesis that the ammonia formation in the body takes place in the kidneys.

S. S. Z.

**The Inorganic Constituents of the Blood-serum in Nephritis.** W. DENIS and S. HOBSON (*J. Biol. Chem.*, 1923, 55, 183—190).—The sera of twenty-two patients suffering from nephritis and cardiorenal disease have been analysed for non-protein nitrogen, creatinine, uric acid, and inorganic constituents. No marked regularity in the results has been observed. In many cases, a high value was obtained for the sulphate-ion, which appears to be excreted with more difficulty than any other inorganic radicle normally present in the blood.

E. S.

**Analysis of Bone Ash in Cases of War Osteopathy.** WILHELM LOLL (*Biochem. Z.*, 1923, 135, 493—503).—An analysis has been made of the bones of four severe cases of war osteopathy. Normal human bones contain CaO, 51.8—52.1%, MgO, 0.78—0.85%, and P<sub>2</sub>O<sub>5</sub>, 38.8%. In war osteopathy, the ribs and pelvis contain CaO, 56.8—76.8%, MgO, 0.74—0.8%, and P<sub>2</sub>O<sub>5</sub>, 16.2—37.3%. The composition of the tibia was nearly normal.

H. K.

**Experimental Tetany. I. Distribution of Calcium in the Plasma and Cells. II. Variation in Colloidal and Ionic Calcium.** E. W. H. CRICKSHANK (*Biochem. J.*, 1923, 17, 13—29).—An immediate state of alkalosis which is not necessarily marked follows parathyroidectomy and with the onset of severe tetany it passes rapidly into a condition of acidosis. There is an immediate relief of the condition in dogs on withdrawing 70—100 c.c. of blood, which suggests a toxic causative factor. In tetany there was observed a loss of calcium amounting to 37.2% for whole blood, 54.4% for the cells, and 35.2% for the plasma. The diffusible calcium in sera of parathyroid tetanic animals amounted to 94% of the total calcium, whilst in the serum of normal animals the diffusible calcium was only 60—70% of the total calcium. The author concludes that the calcium deficiency and the great loss of colloidal calcium are due to a rapid protein disintegration.

S. S. Z.

**The Physiological Action of Amino-acid Esters.** MINORU ARAI (*Biochem. Z.*, 1923, 136, 203—212).—The physiological actions of histidine methyl ester, tyrosine ethyl ester, *dl*-phenyl-alanine ethyl ester, *l*-leucine ethyl ester, *l*-cystine ethyl ester, and glycine ethyl ester have been examined. In general, the action is weak. On the blood-pressure, they may have a pressor or depressor effect, depending on the animal used, and on the isolated uterus they have a stimulating action. The actions are similar to those of the corresponding amines.

H. K.

**Hydrolysis of Amides in the Animal Body. The Comparative Stability of Surface Active Homologues in Relation to the Mechanism of Enzyme Action.** CYRUS H. FISKE (*J. Biol. Chem.*, 1923, 55, 191—220).—Acetamide, propionamide, *n*-butyramide, and *n*-valeramide were injected subcutaneously into cats and the amount of unchanged amide excreted in the urine estimated in each case. The results indicate that the rate of hydrolysis of amides in the animal organism increases with the length of the carbon chain, the order of stability *in vivo* thus being the reverse of that shown *in vitro*. Attention is directed to other reactions (hydrolysis of esters, oxidative processes) in which a similar relation holds. Since the tendency to adsorption of homologous compounds increases with the length of the carbon chain, it is suggested that the greater reactivity in the body of the higher homologues is due to the greater ease with which they are adsorbed by enzymes.

E. S.

**The Relation between the Chemical Constitution of Proteinogenous Amines and their Effect on Body Temperature and Blood Pressure.** M. CLOETTA and F. WÜNSCHE (*Arch. exp. Path. Pharm.*, 1923, 96, 307—329).—The following new substances have been obtained: ethyl carbethoxyglutamate; carbethoxyglutamodiamide, m. p. 179° (corr.); pyroglutaminamide, glistening scales, m. p. 103° (corr.); diacetyltyrosine ethyl ester, fine white needles, m. p. 86° (corr.); dicarbethoxytyrosine, m. p. 97° (corr.); diacetyltyramine, m. p. 103° (corr.); carbethoxytyramine, m. p. 80—81° (corr.); nitrotyramine, a yellow powder, m. p. 210°

(corr.); *aminotyramine*, long, white crystals, m. p. 225° (decomp.); *p-hydroxyphenylethylcarbamide*, glistening, white scales, m. p. 132° (corr.). The effect of these and other substances on body temperature and blood pressure has been investigated. W. O. K.

**Influence of Aliphatic Narcotics on the Swelling of Cell Colloids.** M. KOCHMANN (*Biochem. Z.*, 1923, 136, 49—65).—The action of the first five normal chain aliphatic alcohols, of chloral hydrate, urethane, chloroform, and ether on the swelling of finely powdered fibrin and on the gastrocnemius muscle of the frog has been examined in relation to narcosis. The order in which the narcotics inhibit the swelling of fibrin particles is approximately the same as the order of their narcotic activity towards the electrically stimulated gastrocnemius muscle. The results support the theory of narcosis that narcotics change the permeability of the cells by removal of water. H. K.

## Chemistry of Vegetable Physiology and Agriculture.

**The Botulinus Toxin.** KONRAD SCHÜBEL (*Arch. exp. Path. Pharm.*, 1923, 96, 193—259).—When cultivated in a bouillon medium, *Bacillus botulinus* gives rise to gaseous products, amongst which carbon dioxide, hydrogen sulphide, and hydrogen have been identified. At the same time, the medium becomes distinctly acid owing to the production of *n*-butyric acid and small quantities of other organic acids. In addition to these products, butyl alcohol, isobutyl alcohol, ammonia, and trimethylamine have been isolated; qualitative tests indicating the presence of small quantities of an aldehyde have also been obtained. From the quantitative results, the author concludes that the dextrose contained in the medium is decomposed mainly into butyl alcohol and butyric acid, according to the equation  $2C_6H_{12}O_6 = C_4H_8O_2 + C_4H_{10}O + 4CO_2 + 2H_2 + H_2O$ .

The botulinus toxin may be partly separated from colloidal material by ultra-filtration. It is insoluble in alcohol, acetone, chloroform, or ether, is readily destroyed by boiling its solution for a few moments, but is stable to air and light. Alkalis destroy it more readily than hydrochloric acid; concentrations of 0.91% of the latter are necessary for destructive effects to become apparent. The toxin is precipitated from solution by salts of the heavy metals, by certain protein and alkaloid precipitants, and by saturation with ammonium sulphate. It is adsorbed by animal charcoal and by certain inorganic colloids; its behaviour in this respect suggests that it possesses a negative charge. It dialyses readily through parchment and collodion membranes, its toxic properties being thereby apparently increased. Pepsin and trypsin are without action on it.

The pharmacological action of the toxin has also been investigated. E. S.

**The Formation of Dextrorotatory  $\beta$ -Furyl-lactic Acid by *Bacillus proteus*.** TAKAOKI SASAKI and ICHIRO OTSUKO (*Biochem. Z.*, 1923, **135**, 504—505; cf. A., 1922, i, 302).—d- $\beta$ -Furyl-lactic acid is formed in small yield by the action of *Bacillus proteus* on dl- $\beta$ -furylalanine. It has m. p. 95—96° and  $[\alpha]_D^{25} + 27.36^\circ$  in water.

H. K.

**Formation of Mercaptan from l-Cystine by *Bacteria*.** MASATOSHI KONDO (*Biochem. Z.*, 1923, **136**, 198—202).—*Proteus vulgaris* produces mercaptan from l-cystine in presence of lactose, dextrose, sucrose, glycerol, and histidine, but *Bacillus coli* is variable in its action. Both, however, produce hydrogen sulphide from l-cystine, and also probably ethyl sulphide.

H. K.

**Culture of *Bacillus pyocyaneus* on Definite Chemical Media.** A. LIOT (*Ann. Inst. Pasteur*, 1923, **37**, 234—274).—*Bacillus pyocyaneus*, which produces normally a blue pigment in the medium on which it is grown, will grow on agar if a suitable source of nitrogen is added. Various substances, such as ammonium salts of monobasic and dibasic fatty acids, amides, amino-acids, and alcohols and sugars, along with inorganic ammonium salts, have been investigated as to their efficiency in producing growth and pigment.

W. O. K.

**The Bactericidal Action of Tellurium Derivatives of certain Aliphatic  $\beta$ -Diketones.** GILBERT THOMAS MORGAN, EVELYN ASHLEY COOPER, and ARNOLD WIGHAM BURTT (*Biochem. J.*, 1923, **17**, 30—33).—A series of tellurium derivatives of aliphatic  $\beta$ -diketones has been tried with the purpose of ascertaining the influence of chemical constitution on the germicidal power of these compounds, and also their specific action on different micro-organisms. It is found that the bactericidal action increases considerably as the homologous series is ascended, until with a third substitution of the methyl group a limit is reached beyond which there may even be a diminution in the germicidal action.

The bactericidal action of the compounds is determined by the chemical structure of the  $\beta$ -diketone, position isomerism being a determining factor. Experiments with various organisms have disclosed that the above compounds exert a selective action on the coliform organisms. Cocci are more resistant to them. S. S. Z.

**Stimulation of Alcoholic Fermentation by Chemically Defined Substances.** T. SODA (*Biochem. Z.*, 1923, **135**, 610—620).—Cell-free fermentation of dextrose is accelerated by trimethylamine oxide, allyl alcohol, cinnamyl alcohol,  $\alpha$ -crotonic acid,  $\alpha\alpha'$ -diketopimelic acid, benzoylacetone, and  $\alpha$ -methylhexanone.

H. K.

**Enzymes. II.** A. VON EULER and KARL MYRBÄCK (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 22, 1—31).—A study, in the first place, of the autofermentation (as distinct from autolysis) of fresh bottom-yeast. Autofermentation is accelerated by toluene, but retarded if ethyl acetate is also added, more particularly in

presence of dextrose. Chloroform also inhibits the process. With dried yeast, autofermentation is inhibited by mixtures of toluene and ethyl acetate, either in presence or in absence of dextrose. The latter substance, in presence of phosphate ( $p_H$  5), retards the process, as also does sodium chloride. The inhibiting effect of toluene is more marked in presence of yeast-gum, which is itself unaffected.\*

The fermentation of dextrose by dried yeast, in presence of phosphate, is practically unaffected by the addition of lactose, which is not appreciably fermented. Lactose or toluene, or mixtures of these two substances, inhibit the autofermentation of dried yeast. Complete hydrolysis of dried yeast, before and after autofermentation, shows a loss of dextrose constituents corresponding with the carbon dioxide produced.

The second section of the paper deals with the purification and adsorption of saccharase along the lines laid down by Willstätter and Racke (A., 1921, i, 823). The results of the latter authors are confirmed in connexion with autolysis, acetone and alcohol precipitation, adsorption by aluminium hydroxide and kaolin, etc. Kieselguhr does not adsorb saccharase.

In the third section of the paper, it is shown that the inactivating effect on saccharase solutions of *p*-phenylenediamine and formaldehyde depends on the hydrogen-ion concentration (cf. Rona and Bloch, A., 1922, i, 65).  
E. E. T.

**Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. V. Formation of Glycerol when the Intermediate Acetaldehyde is Retained by Animal Charcoal.** EMIL ABDERHALDEN and SUSI GLAUBACH (*Fermentforsch.*, 1922, 6, 143—148).—Neuberg's observation that acetaldehyde forms an intermediate stage in the degradation of dextrose to alcohol and carbon dioxide by means of the enzymic complex, zymase, is now supplemented by the discovery that the fixation of acetaldehyde from a fermenting or fermented solution by means of animal charcoal (A., 1922, i, 92) is accompanied by increase in the amount of glycerol formed. The extent of such increase is augmented when the quantity of charcoal present is increased.  
T. H. P.

**Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. VI.** EMIL ABDERHALDEN (*Fermentforsch.*, 1922, 6, 149—161).—The influence of various substances on alcoholic fermentation (cf. Neuberg and Sandberg, A., 1922, i, 408) is as follows. Yeast maceration juice dialysate: first dialysate accelerating, second dialysate, retarding; tyrosine, at first retarding, later accelerating; di-iodotyrosine, at first accelerating, later retarding; dihydroxyphenylalanine, accelerating in small, retarding in large, doses; cystine in large doses, greatly accelerating at first and retarding later, but in smaller doses, accelerating; cysteine at first retarding but afterwards considerably accelerating; tryptophan, histidine, and, especially, arginine, accelerating; caffeine, at first accelerating, later retarding, the reverse being the case with allantoin; xanthine, or *dl*-adrenaline, greatly accelerating; diethyl-

amine, retarding; cholesterol, or homovanillin, at first retarding, later accelerating; vanillin, choline, acetylcholine, retarding.

T. H. P.

**Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. VII. Influence of Animal Charcoal and other Substances on the Time-course of Alcoholic Fermentation.** EMIL ABDERHALDEN (*Fermentforsch.*, 1922, 6, 162—171).—Animal charcoal accelerates alcoholic fermentation of sugar solution to a more marked extent than either dipotassium hydrogen phosphate or sodium laevulosediphosphate, the acceleration being still further increased by use of the charcoal and one of these phosphates together. The very great retardation of the fermentation produced by toluene almost entirely disappears if animal charcoal also is present; adsorption of the toluene by the charcoal appears to be the cause of this protective action of the charcoal. The effect of toluene on fermentation by dried yeast is far less marked than when fresh yeast is used.

The initial stimulation of fermentation by dried yeast sometimes caused by toluene is confirmed, but not explained. Especially in presence of animal charcoal, toluene produces a very marked acceleration of the rate at which carbon dioxide is liberated from pyruvic acid by dried yeast.

T. H. P.

**Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. VIII. Formation of Glycerol when the Intermediate Acetaldehyde is Retained by Animal Charcoal.** EMIL ABDERHALDEN and WALTER STIX (*Fermentforsch.*, 1922, 6, 345—347).—The proportion of glycerol formed during the fermentation of dextrose by yeast may be considerably increased by increase of the amount of animal charcoal present and by expelling the air from the fermentation vessel by means of carbon dioxide (cf. Abderhalden and Glaubach, preceding page).

T. H. P.

**Adsorption of Acetaldehyde and Pyruvic Acid, Separately and Together, by Animal Charcoal and Other Adsorbents.** EMIL ABDERHALDEN and HIDEKI SUZUKI (*Fermentforsch.*, 1922, 6, 137—142).—The amount of acetaldehyde or pyruvic acid adsorbed from aqueous solutions by a certain weight of animal charcoal under definite conditions increases with, but less rapidly than, the concentration of the solution. That the action represents a true reversible adsorption is shown by the results of equilibrium experiments. It appears, but it is not yet certain, that part of the adsorbed acetaldehyde undergoes change at the surface of the charcoal. When both acetaldehyde and pyruvic acid are present in solution, the amount of each adsorbed by the charcoal is diminished (cf. Abderhalden, A., 1922, i, 92; Grab, A., 1922, i, 306; Abderhalden and Glaubach, preceding page).

T. H. P.

**Formation of Citric Acid in Cultures of *Aspergillus niger* and *Penicillium glaucum* on Sugar.** WL. BUTKEWITSCH (*Biochem. Z.*, 1923, 136, 224—237).—When *Aspergillus niger* and

*Citromyces glaber* were grown on media containing sucrose in presence of calcium carbonate, citric and oxalic acids accumulate much more rapidly in the case of the former than the latter. This also happens if there be available a plentiful source of nitrogen. Evidence is adduced to show that a soluble calcium salt is formed in these solutions, but the acid has not yet been isolated. *Penicillium glaucum* is also able to produce small quantities of citric and oxalic acids in culture media of sucrose and calcium carbonate. H. K.

**The Carbamide Content of Fungi.** NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 136, 1—8).—The carbamide content of fungi varies not only from genus to genus, but also among the species of a genus, *Lycopodon echinatum*, containing 1.26% and *L. gemmatum*, 10.7%, of carbamide on the dried material. The genera *Psalliota* and *Pholiota* also show similar variations. The carbamide content increases to a maximum at the beginning of ripening, but then falls off to nothing when fully ripe. H. K.

**Formation of Carbamide in Fungi.** NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 136, 9—19).—During ripening, fungi treated with ammonia compounds can convert ammonia into carbamide. This takes place even if the mycelium be detached. The carbamide functions, it is thought, as a nitrogenous reserve substance. H. K.

**Comparative Studies on Respiration. XXIV. The Effects of Chloroform on the Respiration of Dead and of Living Tissue.** GEORGE B. RAY (*J. Gen. Physiol.*, 1923, 5, 469—477).—The rate of production of carbon dioxide by living and by dead *Ulva*, a green marine alga, in the presence of chloroform, has been investigated, and the influence of ferric sulphate and hydrogen peroxide determined. W. O. K.

**The Biological Action of Röntgen Rays. III.** EUGEN PETRY (*Biochem. Z.*, 1923, 135, 353—383).—Seed embryos submitted to the action of a number of oxidising agents are not thereby rendered more or less sensitive to Röntgen radiation. The only oxidising agent which confers greater sensitiveness is hydrogen peroxide. H. K.

**Chemical Constituents of Green Plants. XXIV. Citric Acid.** HARTWIG FRANZEN and FRITZ HELWERT (*Biochem. Z.*, 1923, 135, 384—415).—From a critical survey of the available literature on the occurrence of citric acid in plants, the authors conclude that the generally accepted view that citric acid is widely distributed is erroneous, as in many cases the identification is insufficient. H. K.

**Chemical Constituents of Green Plants. XXVI. Tartaric Acid.** HARTWIG FRANZEN and FRITZ HELWERT (*Biochem. Z.*, 1923, 136, 291—305).—A critical survey of the literature on the recorded occurrence of tartaric acid in eighty-two plants leads to the conclusion that tartaric acid only occurs with certainty in five,

*Vitis vinifera* (berries), *Tamarindus indica* (fruit), *Beta vulgaris* (unripe beet), *Acer saccharinum* (juice), and *Pyrus aucuparia* (berries). It also, probably, occurs in *Quercus pedunculata*. H. K.

**The Formation of Vitamin-A in Plant-tissues. II.** KATHARINE HOPE COWARD (*Biochem. J.*, 1923, 17, 134—144; cf. i., 1921, i, 837).—Light is necessary for the formation of vitamin-A in plant-tissues. Ultra-violet rays of the spectrum are not essential, and the formation of the vitamin can take place under the influence of electric light in the absence of sunlight. The process of vitamin-A synthesis can be carried on in the absence of carbon dioxide and of oxygen in the surrounding atmosphere, and is independent of the presence of chlorophyll in the plant. The presence of chloroform in the atmosphere, however, prevents the formation of the vitamin. Almost complete absence of calcium salts from the nutrient solution of a water culture of *Tradescantia* does not prevent the synthesis of vitamin-A in the leaves of the plant. S. S. Z.

**The Association of Vitamin-A with Lipochromes of Plant tissues.** KATHARINE HOPE COWARD (*Biochem. J.*, 1923, 17, 45—156).—Some lipochrome (generally carotene) is always associated with the vitamin in plant-tissues and consequently the presence of carotene, particularly carotene exposed to sunlight, suggests the presence of vitamin-A also. S. S. Z.

**Hydrocyanic Acid in Burmah Beans (*Phaseolus lunatus*).** F. CHARLTON (*Agric. Res. Inst. Pusa Bull.*, 140, 7 pp.).—The amount of hydrocyanic acid liberated by enzyme action in Burmah beans increases with the age of the bean. The elaboration of enzymes in the beans therefore probably continues after the normal ripening process is complete. H. C. R.

**Influence of Sulphur Dioxide on the Respiration of Phanerogams.** JULIUS STOKLASA [with J. ŠEBOR, V. ZDOBŮČEK, and V. NEKOLA] (*Biochem. Z.*, 1923, 136, 306—326).—As a result of comparative experiments on young pines, it is found that small quantities of sulphur dioxide cause a diminution of the carbon dioxide output. The larger the content of sulphur dioxide, the less the respiratory activity. The pine needles show at the same time a bleaching of the chloroplasts. H. K.

**The Mobilisation of Mineral Substances and of Nitrogen in the Bark and Wood in Spring Growth.** AUGUST RIPPPEL (*Biochem. Z.*, 1923, 135, 518—531).—During sprouting of shoots of *Sambucus nigra*, the potassium, phosphorus, and nitrogen are strongly mobilised, the magnesium and sodium to a lesser extent, and calcium, sulphur, and chlorine scarcely at all. The potassium content of the wood increased by 28% after sprouting. H. K.

**Walnut Oil.** KAZUO MATSUMOTO and YOSHISUKE UYEDA (*J. Chem. Ind. Japan*, 1922, 25, 1438—1440).—The fruit of the walnut (*Juglans Sieboldiana*) produced in the Prefecture of Ishikawa

gave 26.54% of kernel, from which 59.58% of oil was obtained by pressure. The oil is light yellow in colour and without odour, and shows the properties of a drying oil:  $d_{40}^{15}$  0.9332,  $n_D^{20}$  1.4800, acid value 0.68, Hehner value 92.3, saponification value 190.1, Reichert-Meissl value 0.62, and iodine value (Hübl) 150.8. K. K.

**Amino-acids of Feeding Stuffs. II. Amino-acids of Linseed Meal, Wheat Bran, Soja Beans, and Red Clover Hay.** T. S. HAMILTON, N. UYEL, J. B. BAKER, and H. S. GRINDLEY (*J. Amer. Chem. Soc.*, 1923, 45, 815—819; cf. A., 1923, ii, 93).—The amino-acid contents are tabulated of linseed meal, wheat bran, soja beans, and red clover hay, and of other foodstuffs already investigated, as estimated by the modified Van Slyke method previously described. [Cf. *J.S.C.I.*, 1923, 418A.] W. S. N.

**The Potassium-Nitrogen Ratio of Red Clover as Influenced by Potassium Fertilisers.** PAUL EMERSON and JOHN BARTON (*J. Amer. Soc. Agron.*, 1922, 14, 182—192).—The solubility of soil potassium, as indicated by absorption by the plant, is increased by applications of manure, acid phosphate, or combinations of both. The ability of red clover to take up potassium varies with the kind of compound supplied; for instance, the potassium of kainite is more easily absorbed than that of potassium chloride or sulphate. Calcium carbonate, when applied to an acid soil, appears not to affect the solubility of native soil potassium, but may possibly over-stimulate nitrate production. The potassium: nitrogen ratio is widened slightly by applications of lime, but narrowed by applications of manure or acid phosphate, or both, in the presence of lime.

CHEMICAL ABSTRACTS.

**Disappearance of Nitrates from Soil under Timothy Grass.** J. A. BIZZELL (*J. Amer. Soc. Agron.*, 1922, 14, 320—336).—The addition of sodium nitrate to timothy grass sod in early spring is followed by a rapid disappearance of the nitrate from the 20 cm. of surface soil; this disappearance is due only in part to the absorption of nitrogen by the growing crop. Leaching or denitrification apparently did not remove the nitrogen from the soil. Various organisms of the soil evidently transformed the nitrate into ammonia or into some form of organic combination.

CHEMICAL ABSTRACTS.

**Hydrogen-ion Concentration of the Soil and its Significance to the Vegetation, especially to the Natural Distribution of Plants.** CARSTEN OLSEN (*Compt. rend. Trav. Lab. Carlsberg*, 1923, 15, 1—166).—The object was to ascertain to what extent the natural flora of soils is affected by the hydrogen-ion concentration, and whether the effect is direct or caused by secondary changes. Botanical analyses of natural vegetation were compared with the reaction of the soils on which it grew. Individual species were found only to occur on soils having a definite range of  $pH$  values. Within this range is a narrower one in which the species appeared with the greatest average frequency. The number of

species and their frequency of occurrence is greatest on nearly neutral soils. Increased  $p_H$  value corresponds with a decrease in the number of species and their density. In water culture solutions, acid-soil plants grow best in media of  $p_H$  4; whilst plants characteristic of neutral and alkaline soils are favoured by nutrient solutions with  $p_H$  6—7. Typical acid-loving plants show poor growth and became chlorotic when grown in culture solutions which are only faintly acid. The theory that the apparent toxicity of acid soils (Hartwell and Pember, *Soil Sci.*, 1914, 6, 259) is due to soluble aluminium salts is not confirmed. Alkaline-soil plants were not injured by small amounts of aluminium salts. The acid-soil plants are not characterised by the power of utilising ammonium salts. Both acid- and alkaline-soil plants are nourished equally well by ammonium salts and by nitrates. Acid-soils cannot be differentiated from normal ones on account of their lack of nutrients. The flora of a rich acid-soil bear no resemblance to those of a poor alkaline soil. It is concluded that the hydrogen-ion concentration of a soil directly, and to a considerable extent, affects the nature of the vegetation growing upon it.

A. G. P.

**Influence of Hydrogen-ion Concentration on the Adsorption of Plant Food by Soil Colloids.** E. B. STARKEY and NEIL E. GORDON (*Soil Sci.*, 1922, 14, 449—457).—The adsorption by silica and ferric hydroxide gels of various plant nutrients was determined. The adsorption of cations was generally greater with increasing  $p_H$  values. Anions were adsorbed in the following order: phosphate, sulphate, nitrate. Acidity increased the adsorption of phosphate but the adsorption of sulphates and nitrates was scarcely affected by the reaction of the medium. Ferric hydroxide gel was a considerably more active absorbent than silica gel. Near the neutral point, slight changes in  $p_H$  values caused relatively large changes in the adsorption of potassium-ions.

A. G. P.

#### Factors Affecting the Soil Reaction. I. Soil-Water Ratio.

ROBERT M. SALTER and M. FRANCIS MORGAN (*J. Physical Chem.*, 1923, 27, 117—140).—The hydrogen-ion concentration of nine acid soils has been determined at soil-water ratios from 1:1 to 1:3125 by the hydrogen electrode method. The velocity of hydrolysis of sucrose by five of the same soils of soil-water ratio between 1:0.0894 and 1:625 has also been determined. Both methods of determination show that the hydrogen-ion concentration varies systematically with the soil-water ratio, the highest hydrogen-ion concentration occurring at high soil-water ratios, with a progressive decrease as the dilution is increased. In general, the changes in hydrogen-ion concentration at varying soil-water ratios agree with the distribution of hydrogen-ions between soil and solution, which could be expected if controlled by an adsorption mechanism. A slight tendency is noted with all soils to deviate from the theoretical adsorption values over a restricted range of dilution. With two of the nine soils examined, this deviation was sufficient to prevent the determination of a theoretical equation which would describe

the variation in hydrogen-ion concentrations observed. On the basis of the results obtained, it appears that the reaction of a soil is dependent mainly on the total dissociated acid present and to a lesser extent on the adsorptive capacity of the soil for hydrogen-ions and the soil-water ratio. It is urged that the soil-water ratio should be stated in all results on hydrogen-ion measurements of soils and that one of the ratios, 1:5, 1:25, or 1:125, should be chosen as a standard.

J. F. S.

**Relations Between the Active Acidity and Lime Requirement of Soils.** EDGAR T. WHERRY (*J. Wash. Acad. Sci.*, 1923, 13, 97—102).—A correlation coefficient is employed to express the relationship between soil acidity and lime requirement, based on the equation lime requirement =  $C \times (\text{Specific acidity} - 1)$ . (For "Specific acidity" see Wherry, *ibid.*, 1920, 9, 305.) Values of  $C$  are calculated from published data, and are shown to vary to so great an extent with soil type and treatment that no calculations of lime requirement from it seem practicable. The coefficient  $C$  is believed to be a measure of the adsorptive power of soils for the hydrogen-ion, and may be used as a basis for a rough classification of soils.

A. G. P.

**Catalytic Action of Soils.** SHIGERU OSUGI (*Ber. Ohara Inst. landw. Forsch.*, 1922, 2, 197—218).—The power of soils to decompose hydrogen peroxide would appear to be associated with humus, ferric compounds, and manganese compounds, although no relationship between catalytic power and the soil content of these substances was found. Soil catalysis was increased by coagulating agents and decreased by peptisation.

The reaction of the soil may influence its catalytic power directly, and also as a result of its effect on the physical state of the soil particles. The effect of bacteria on soil catalysis is small, and that of enzymes larger, but the organic and inorganic soil constituent are the most important factors.

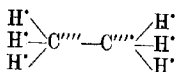
A. G. P.

**Adsorption of Plant Food by Colloidal Silica.** R. C. WILEY and NEIL E. GORDON (*Soil Sci.*, 1922, 14, 441—447).—The adsorption of various plant foods was determined by shaking with silica hydrosol and hydrogel. Negative adsorptions may be due either to the water being more strongly adsorbed than the dissolved salts, or to the fact that the water of hydration does not all act as a homogeneous solvent, or to lower concentrations existing in the finer capillaries. In general, metals are negatively adsorbed by both gel and sol. Nitrates and sulphates are negatively adsorbed to a slight degree. The phosphate radicle is positively adsorbed by the gel, and negatively by the sol. In the former case, more phosphate was adsorbed than the radicle with which it was associated, and, moreover, was extremely difficult to wash out.

A. G. P.

## Organic Chemistry.

**The Foundations of an Electronic Theory of Organic Chemistry.** A. M. BERKENHEIM (*J. Russ. Phys. Chem. Soc.*, 1917, 49, [ii], 1—181).—A theoretical paper in which an attempt is made to apply J. J. Thomson's and Stark's views of the structure of the atom to explain the reactions of carbon compounds. It is suggested that the neutral carbon atom acquires positive or negative polarity according to whether it parts with one or more electrons on becoming connected with other atoms or, conversely, acquires one or more electrons in the process; this polarity of the carbon atom then determines its reactions. Ethane is represented as



and acetylene as  $\text{H} \cdot \text{C}^{''''} - \text{C}^{''''} \text{H} \cdot$ ; a large number of organic reactions is discussed and shown to support the theory.

G. A. R. K.

**Low Temperature Tar. II.** FRANZ SCHÜTZ, WILHELM BUSCHMANN, and HEINRICH WISSEBACH (*Ber.*, 1923, 56, [B], 869—874; cf. this vol., i, 195).—The communication deals mainly with the components of the light oils which boil below 75°.

The isolation of the paraffin hydrocarbons is effected by treatment of the various fractions with concentrated sulphuric acid and examination of the unabsorbed and non-polymerised portions. The fraction, b. p. up to 10°, contains *n*-butane (4%), that of b. p. 15—35° contains methylbutane, b. p. 17—18° (2.4%), and *n*-pentane (5.1%). Methylpentane, b. p. 62—63° (18%), and *n*-hexane (24%) are, respectively, present in the fractions of b. p. 53° and 68—72°, whereas *n*-heptane (21%) and *n*-octane (1%) are found in those of b. p. 98—102° and 120—130°. The isolation of the paraffins from the fractions of higher boiling point is particularly difficult, since the aromatic hydrocarbons largely predominate. Heptane is possibly present in the benzene fraction, b. p. 77—78.5°.

The identification of the unsaturated hydrocarbons is effected by preliminary fractional distillation within very narrow limits, followed by treatment of the individual fractions with bromine and isolation of the bromides. Ethylene, propylene,  $\Delta^2$ -butylene,  $\Delta^3$ -butylene, and  $\Delta^2$ -pentene are thus shown to be present. *cyclo*-Pentadiene is shown to occur to the extent of 5—7% in the fraction, b. p. 40°, and is identified by conversion into dimethylfulvene, b. p. 154—155°.

The first runnings of the light oil contain acetaldehyde in addition to acetone, whilst methyl ethyl ketone and acetonitrile are present

in the benzene fraction. Methyl mercaptan and dimethyl sulphide are also found in the first runnings. The fraction, b. p. 20–40°, contains carbon disulphide in very small amount. H. W.

**Lignite Low Temperature Tar.** E. FROMM and H. ECKARD (*Ber.*, 1923, 56, [B], 948–953).—The low temperature tars obtained in rotary furnaces from two geologically similar lignites, termed, respectively, "Louise" and "Grefrath," obtained from the neighbourhood of Cologne have been investigated; they exhibit peculiar differences, which are possibly due to differences in botanical origin.

The neutral components of the "Louise" tar which are volatile with steam, have boiling points 140–240°, and the densities of the individual fractions increase regularly from 0.835 to 0.895. They appear to be mixtures of unsaturated hydrocarbons and oxygenated substances. The similarly obtained components of the "Grefrath" tar have b. p. 115–240°,  $d$  0.819–0.897, and give a portion, b. p. 115–160°,  $d$  0.823–0.832, which contains an ether and a terpene-like compound,  $C_{10}H_{18}$  or  $C_{11}H_{20}$ , b. p. 185°,  $d$  0.8659.

The neutral components of the "Louise" tar which are not volatile with steam consist of a mixture of paraffins which is separated by fractional distillation and subsequent crystallisation into the following individuals, which are assumed to belong to the normal series:  $C_{23}H_{48}$ , m. p. 46°;  $C_{24}H_{50}$ , m. p. 52°;  $C_{25}H_{52}$ , m. p. 57.5°;  $C_{26}H_{54}$ , m. p. 62°;  $C_{27}H_{56}$ , m. p. 69.6°;  $C_{28}H_{58}$ , m. p. 73°. The occurrence of the first member is remarkable, since only hydrocarbons with an even number of carbon atoms have been isolated previously from tars.

The basic portions of the "Louise" tar which are volatile with steam contain a yellowish-brown oil from which a benzoyl derivative, m. p. 36°, could be obtained in small amount, and pyridine which is identified as its additive product with mercuric chloride, m. p. 194°. The presence of pyridine in the similarly isolated fraction of the "Grefrath" tar could not be detected; by treatment of it with aqueous oxalic acid it was, however, found possible to isolate an oxalate, m. p. 177–178°, which is possibly derived from methylpyridine.

The acidic components which are volatile with steam contain only traces of carboxylic acids. The phenols are subdivided by fractional distillation under diminished pressure and analysed as their phenylurethanes. *m*-Cresol is the only substance of this class which could be identified with certainty; it is present in the "Grefrath" tar. Several phenols,  $C_6H_5OH$ , and a phenol,  $C_9H_{11}OH$ , are also present, the phenylurethanes of which are not apparently identical with any known compounds of this class. H. W.

**$\beta$ -Methyl- $\Delta^5$ -pentene.** H. VAN RISSEGHEN (*Bull. Soc. chim. Belg.*, 1923, 32, 144–150).—The hydrocarbon was prepared by condensation of acetic and butyric acids to methyl propyl ketone (pentane- $\gamma$ -one), which, on treatment with magnesium methyl

iodide, yielded a hexanol; this was then dehydrated by means of toluene-*p*-sulphonic acid. A second method, dehydration of  $\delta$ -methylbutyl alcohol, was also used.  $\beta$ -Methyl- $\Delta^2$ -pentene so obtained forms an additive product with bromine, and yields propaldehyde, acetone, and propionic acid on oxidation. It has b. p. 66.7—67.1°/760 mm., m. p. —134.75°;  $d_4^{20}$  0.7051,  $d_4^{15}$  0.69145,  $n_D^{15}$  1.4003,  $n_D^{15}$  1.4093,  $n_D^{15}$  1.4144,  $n_D^{15}$  1.4028. The bromo-derivative has b. p. 69.5—70.5°/14 mm., m. p. —54.49°;  $d_4^{15}$  1.6024,  $n_D^{15}$  1.5825,  $n_D^{15}$  1.50294,  $n_D^{15}$  1.51473,  $n_D^{15}$  1.52144,  $n_D^{15}$  1.506225. The action of chlorine on the hydrocarbon results in the formation of an additive product together with a more halogenated chloro-substitution compound and a derivative resulting from the fixation of one molecule of hydrogen chloride on the double bond.

H. J. E.

**Action of Bromine on Hydrocarbons.** B. K. MERESHOWSKY (*Annalen*, 1923, **431**, 113—132).—It is shown from the author's experiments and previous work on this subject that specific catalysts not only influence the rate and initial direction of halogenation, but also determine the simultaneous production of different end-products, if the reaction is allowed to continue; the production of polyhalogenated isomerides may therefore be selectively catalysed. The catalysts used are shown to form the following series, in the order of decreasing production of the more symmetrical isomeride: (1) pure bromine without a catalyst, (2) metallic iron, (3) metallic aluminium or aluminium tribromide, (4) ferric bromide. The substitution rules of Markovnikov, Städel, and V. Meyer are combined and extended as follows. (1) If the number of carbon atoms in the hydrocarbon is  $n$ , then, either with or without a catalyst at temperatures below 100°,  $n-1$  halogen atoms will become successively attached to carbon atoms on which substitution has not yet occurred. (2) If  $n-1$  atoms of the hydrocarbon already carry a halogen atom, a further halogen atom will enter partly on the remaining halogen-free carbon atom, and partly on that one of the other carbon atoms which carries the greatest number of hydrogen atoms. (3) Further substitution generally occurs on the carbon atom bearing the greatest number of hydrogen atoms. (4) Substitution always occurs in several directions, depending on the catalyst.

The action of pure bromine on propylene in the absence of a catalyst gives propylene bromide, 90%, and  $\alpha\beta\gamma$ -tribromopropane, about 4%. In the presence of metallic iron,  $\alpha\beta\gamma$ -tribromopropane and  $\alpha\alpha\beta$ -tribromopropane are formed in the proportion of 40 : 17; with ferric bromide or aluminium, the same compounds are produced in the ratio 8 : 33, and with aluminium bromide in the ratio 1 : 1. In the presence of aluminium a product of higher boiling point, 130—150°/20 mm., is also formed. The action of bromine on isobutylene in the absence of a catalyst at 45—50° leads mainly to the formation of dibromoisobutane, 45%, and of  $\alpha\beta\gamma$ -tribromoisobutane, m. p. —32°, b. p. 222—225°/75 mm. (Pogorschelsky, *A.*, 1905, i, 315), 44%, together with smaller amounts of tetra-

bromo-, pentabromo-, and hexabromo-derivatives. In the presence of metallic iron, the above is the only tribromo-derivative produced, but the use of ferric bromide leads to the formation of  $\alpha\alpha\beta$ -tribromoisobutane and  $\alpha\beta\gamma$ -tribromoisobutane in the ratio 31:11; the former gives  $\alpha\alpha$ -dibromoisobutylene,  $\text{CMe}_2\text{CBr}_2$ , the latter  $\alpha$ -bromo- $\gamma$ -acetoxy- $\beta$ -methylpropylene,  $\text{CHBr}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$ , on treatment with potassium acetate. The same tribromo-derivatives are formed in the ratio 3:5 in the presence of aluminium or aluminium tribromide. Two tetrabromo-derivatives are found in the fractions of higher boiling point. (1)  $\alpha\alpha\beta\gamma$ -Tetrabromoisobutane, b. p. 134—136°/14 mm.,  $d_4^{20}$  2.45445, which is converted by heating with potassium acetate into  $\alpha\alpha$ -dibromo- $\gamma$ -acetoxy- $\beta$ -methylpropylene,  $\text{CBr}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$ , b. p. 114°/16 mm.,  $d_4^{20}$  1.75070, which gives  $\alpha\alpha$ -dibromopropenylcarbinol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CBr}_2$ , on hydrolysis. (2)  $\alpha\beta\gamma\delta$ -Tetrabromoisobutane, m. p. 25°, b. p. 150—151°/14 mm.,  $d_4^{20}$  2.55953, the constitution of which is certain, since other possible tetrabromo-derivatives could not be produced from  $\alpha\beta\gamma$ -tribromoisobutane; moreover, the action of potassium acetate and acetic acid gives the bromo-ester,  $\text{CHBr}\cdot\text{C}(\text{CH}_2\cdot\text{OAc})_2$ , b. p. 136°/14 mm.,  $d_4^{20}$  1.45335, from which the glycol,  $\text{CHBr}\cdot\text{C}(\text{CH}_2\cdot\text{OH})_2$ , m. p. -80°, b. p. 158°/16 mm.,  $d_4^{20}$  1.69582, is produced by hydrolysis. Hexabromoisobutane, m. p. 93°, occurs in small amounts in the residue left after the more volatile halides have been distilled in steam. The constitution of  $\alpha\alpha\beta\gamma$ -tetrabromoisobutane is established by its formation by the addition of bromine in ethereal solution to the unsaturated dibromo-derivative,  $\text{CHBr}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{Br}$  (A., 1914, i, 508).  
W. S. N.

**Mechanism of the Reactions of Alkyl Halides.** ADOLF FRANKE and RUDOLF DWORZAK (*Monatsh.*, 1923, 43, 661—671).—The possibility of the intermediate formation of unsaturated compounds during the conversion of bromo- into hydroxy-derivatives, etc. (cf. A., 1914, i, 7), has suggested to the authors to study similar displacements of halogen attached to an asymmetric carbon atom, when, if an optically active derivative is obtained, no intermediate unsaturated compound can have been formed. Active secondary butyl bromide and iodide give an active *mercaptan* on treatment with alcoholic potassium hydrosulphide. The product is converted for purposes of identification, etc., into the mercury derivative, which is shown to be  $\text{C}_4\text{H}_9\text{S}\cdot\text{HgCl}$ , not  $(\text{C}_4\text{H}_9\text{S})_2\text{Hg}$ , the formula given to the corresponding inactive product by Reymann (A., 1875, 141). This author recorded a m. p. 188°, but the present authors obtain no evidence of melting at much higher temperatures.

Potassium hydrosulphide converts  $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethylpropane into the corresponding *dithiol*, which with mercuric chloride gives the compound,  $\text{CMe}_2(\text{CH}_2\cdot\text{S}\cdot\text{HgCl})_2$ .

When optically active *sec*-butyl iodide is heated with aqueous sodium carbonate until it is converted into the alcohol, the latter is inactive. The bromide, on similar treatment, gives a slightly active alcohol.  
E. E. T.

The Labile Nature of the Halogen Atom in Organic Compounds. IX. The Electrical Conductivities and the Reduction of Derivatives of Nitroform. THOMAS HENDERSON, EDMUND LANGLEY HIRST, and ALEXANDER KILLEN MACBETH (T., 1923, 123, 1130—1137).

$\alpha\beta$ -Dinitroethane and the Action of Silver Nitrite on Ethylene Iodide. ALEXEI V. IPATOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 297—303).— $\alpha\beta$ -Di-iodoethane is treated with silver nitrite by Demjanov's method and the mixture of  $\alpha\beta$ -dinitroethane and nitroethyl nitrite thus obtained fractionally distilled. Three fractions are obtained, the first of which, b. p. 70—72°/5 mm., is mainly unchanged  $\alpha\beta$ -di-iodoethane, the second, b. p. 70—78°/5 mm., is a mixture of the latter with nitroethyl nitrite and dinitroethane, whilst the third, b. p. 81—106°/5 mm., is mainly the latter. The  $\alpha\beta$ -dinitroethane thus obtained, b. p. 94—95°/5 mm.,  $d_4^{20}$  1.4597,  $n_D^{20}$  1.4488, forms a tetrabromo-derivative,  $C_2O_4N_2Br_4$ , yellow needles, m. p. 46—47°, and gives on reduction ethylenediamine, the hydrochloride of which sublimes without melting at 208°.

R. T.

The Examination and Dehydration of Methyl Alcohol by Means of Magnesium. NIELS BRERRUM and LÁSZLÓ ZECHMEISTER (*Ber.*, 1923, 56, [B], 894—899).—Clean magnesium reacts vigorously with absolute methyl alcohol at the atmospheric temperature giving magnesium methoxide and hydrogen. The rate at which the latter is evolved is greatly dependent on the water content of the alcohol, which is also indicated by the appearance of the mixture, since magnesium hydroxide is precipitated if water is present. The reaction is given a quantitative form by measuring the time necessary for the evolution of 5, 10, or 20 c.c. of hydrogen under standard conditions and reference to a table which is fully given in the original.

Magnesium is also very suitable for the preparation of anhydrous methyl alcohol. About 10 g. of the clean metal are placed in about a litre of methyl alcohol contained in a distillation apparatus. The reaction speedily becomes so vigorous that the alcohol is brought to its boiling point. When the metal has dissolved, the solution is kept gently boiling during several hours, after which the methyl alcohol is distilled, the first portion of the distillate being rejected. A single treatment usually suffices. It is advantageous to carry out the distillation in a current of dry air. The utility of magnesium is restricted to specimens of methyl alcohol which do not contain more than 0.5—1% of water, but it has the advantage over calcium that it does not introduce ammonia into the alcohol.

Magnesium methoxide,  $Mg(OMe)_2 \cdot 3MeOH$ , crystallises in rhombic plates. At 18° it dissolves in methyl alcohol to the extent of 0.9 mol. per litre.

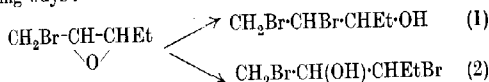
H. W.

Addition of Hydrogen to Acetylene Derivatives. IX. Addition of Hydrogen to Acetylenic  $\gamma$ -Alcohols. J. S. ZALKIND and (MILE) M. A. VILENKINA (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 130—148).—It was observed (A., 1914, ii, 257) that if  $\beta$ -dimethyl- $\Delta^2$ -hexinene- $\beta$ -diol is reduced by the Sabatier method, using as



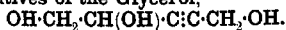
(2) Potassium ethyl sebacate,  $\text{CO}_2\text{Et} \cdot [\text{CH}_2]_{10} \cdot \text{CO}_2\text{K}$ , was electrolysed by the method of Brown and Walker (A., 1891, ii, 1192) to give *n*-hexadecanedicarboxylic ethyl ester,  $\text{CO}_2\text{Et} \cdot [\text{CH}_2]_{14} \cdot \text{CO}_2\text{Et}$  (as a by-product was obtained an acid, b. p. 248–249°, which was identified as  $\Delta^7$ -nonenoic acid,  $\text{CH}_3 \cdot \text{CH} \cdot [\text{CH}_2]_6 \cdot \text{CO}_2\text{H}$ , giving an ester boiling at 226–228° [Brown and Walker gave about 250° for the ester, which is incorrect]). The *n*-hexadecanedicarboxylic ester was reduced by sodium and amyl alcohol to the new glycol,  $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH}_2]_{14} \cdot \text{CH}_2 \cdot \text{OH}$ , which forms white crystals, m. p. 92°, b. p. 238°/13 mm., and on gentle oxidation with permanganate gives the known acid,  $\text{C}_{18}\text{H}_{34}\text{O}_4$ , m. p. 118°. On treatment with sulphuric acid, a new oxide was obtained as a semi-solid, yellow mass, in amount sufficient to purify for analysis: it is probably *ac-oxido-octadecane*,  $\text{H}_3 \cdot [\text{CH}_2]_{12} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$ , since on oxidation with dilute permanganate it yields an acid the silver salt of which, when analysed, gave figures approximating to those required for the salt of myristic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_{12} \cdot \text{CO}_2\text{H}$ . F. A. M.

**Action of Organomagnesium Compounds on the Epibromohydrin of Ethylglycerol.** RAYMOND DELABY (*Compt. rend.*, 1923, 176, 1153–1156).—The action of organic magnesium halides on the epibromohydrin of ethyl glycerol is but little comparable with that on glycerol epibromohydrin, as in the case of both alkyl and aryl magnesium bromides the main reaction consists in the addition of the elements of hydrogen bromide to the epibromohydrin, and only traces of an aryl derivative are formed. The addition of hydrogen bromide might occur in either of the two following ways:



The compound (1) has already been obtained by the addition of bromine to ethylvinylcarbinol (this vol., i, 289) and in the present case it is exclusively the compound (2),  $\alpha\gamma$ -dibromopentan- $\beta$ -ol, b. p. 119–119.5°/23 mm., which is formed. The two compounds were differentiated by the preparation of the picrates of the corresponding tetramethyldiaminopentanol, by oxidation to the corresponding ketones, and conversion of the latter into semicarbazones. The  $\alpha\gamma$ -dibromopentan- $\beta$ -one, b. p. 85–100°/19 mm., reacted with 1 mol. of semicarbazide, giving a ketotriazine by elimination of one of the bromine atoms with a H of the  $\text{NH}_2$ -group. The substance melts at 115–117°. On the other hand, the  $\alpha\beta$ -dibromopentan- $\gamma$ -one reacts with 2 mols. and gives a semicarbazone-ketotriazine, m. p. 229–230°. G. F. M.

#### Some Derivatives of the Glycerol,



ROBERT LESPICHAU (*Compt. rend.*, 1923, 176, 1068–1070).—The oxide of the methyl ether of this glycerol having the constitution

$\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{O} \end{array} \text{CH-CH:CH-CH}_2\text{-OMe}$  was obtained by the action of chloroacetaldehyde on a mixture of magnesium ethyl bromide and methyl propargyl ether. The product was decomposed with acidified water, extracted with ether, and treated with potassium hydroxide, whereby polymerisation products of the aldehyde were resinified and the chlorohydrin was converted into the oxide. It has b. p. 75–76°/15 mm  $d_{20}^{25}$  1.024,  $n_D$  1.4573. By treatment with hydrogen chloride, it is converted into the *chlorohydrin*,  $\text{CH}_2\text{Cl-CH(OH)-CH:CH-CH}_2\text{-OMe}$ , b. p. 117.5–118.5°/12 mm.,  $d_{20}^{21}$  1.1717,  $n_D$  1.4866. Sodium methoxide converts it into the *ether*,  $\text{OMe-CH}_2\text{-CH(OH)-CH:CH-CH}_2\text{-OMe}$ , a liquid, b. p. 119–120°/12 mm.,  $d_{20}^{23}$  1.0508,  $n_D$  1.4608. The ethylene oxide is converted on boiling with water into the glycol ether,

$\text{OH-CH}_2\text{-CH(OH)-CH:CH-CH}_2\text{-OMe}$ ,  
 a thick liquid, b. p. 155–156°/12 mm.,  $d_{20}^{23}$  1.1274,  $n_D$  1.481.  
 Addition of 1 mol. of bromine gives the bromohydrin,  
 $\text{OH-CH}_2\text{-CH(OH)-CBr:CBR-CH}_2\text{-OMe}$ ,  
 a solid melting at 51–52°, b. p. 192°/11 mm. Treatment of this compound with hydrogen bromide at 100° causes demethylation, but the product was not isolated in a pure condition. G. F. M.

**The Preparation of Ethers from Primary Alcohols.** JEAN POPELIER (*Bull. Soc. chim. Belg.*, 1923, **32**, 179–194).—A study of the conditions necessary for the etherification of some primary alcohols in order to obtain a high yield of the corresponding ethers showed that this may be effected by means of a study of the binary mixtures of alcohol and water and the ternary mixtures of alcohol, ether, and water. From a knowledge of the boiling points of these mixtures and the composition of the vapour phase in each case, the preparation of the ethers may be effected with yields of about 90% by simple distillation of the alcohols with sulphuric acid. In general, the process is discontinuous, as adjustments in the composition of the mixture undergoing distillation must be made from time to time. The most suitable proportion of acid varies considerably, according to the alcohol used. Details are given of the application of the method to propyl, butyl, *isobutyl*, amyl, and *isoamyl* alcohols. Formation of unsaturated hydrocarbons may be obviated by working at a sufficiently low temperature.

H. J. E.

**The  $\alpha\alpha'$ -Dichlorodialkyl Sulphides.** FREDERICK GEORGE MANN and (SIR) WILLIAM JACKSON POPE (*T.*, 1923, **123**, 1172–1178).

**Crystal Structure of Basic Glucinum Acetate.** (SIR) W. H. BRAGG (*Nature*, 1923, **111**, 532).—X-Ray analysis shows that the molecule of basic glucinum acetate,  $\text{Gl}_2\text{O(C}_2\text{H}_3\text{O}_2)_6$ , is a perfect tetrahedron, the oxygen atom being at the centre, the glucinum atoms lying on lines from the centre to the corners, and each  $\text{C}_2\text{H}_3\text{O}_2$  group being associated in a symmetrical manner with the edges of the tetrahedron. The crystal structure is that of diamond, a molecule replacing each atom of carbon. A. A. E.

**The Addition of Hydrogen to Acetylenic Acids.** DAVID EMBYS WILLIAMS and THOMAS CAMPBELL JAMES (*Aberystwyth Studies*, 1922, 4, 197—207).—By reduction of phenylpropionic acid with hydrogen in presence of colloidal platinum, Paal and Hartmann obtained *allocinnamic* acid (A., 1909, i, 926) showing that *cis* addition had taken place. Experiments on the same lines with crotonic acid have given similar results, 63% of the theoretical yield of *allo-crotonic* and only 4% of ordinary crotonic acid being obtained. Reduction of acetylenedicarboxylic acid in the same manner, in the form of its normal potassium salt, gave, however, umaric acid without any trace of maleic acid. The addition thus takes place in the *trans* position, and supports the views of Michael A., 1918, i, 249) on the relation between the energy content of such systems and their stereochemical activity. When acetylenedicarboxylic acid is reduced with hydrogen and colloidal platinum in presence of less than two equivalents of alkali, the fumaric acid is further reduced to succinic acid almost as quickly as it is formed.

E. H. R.

**The Constitution of Elaeostearic [Elaeostearic] Acid.** I. VERCRUYSE (*Bull. Soc. chim. Belg.*, 1923, 32, 151—156; cf. Kametaka, T., 1903, 83, 1042; Majima, A., 1909, i, 204).—It has been shown that elaeostearic acid,  $C_{18}H_{32}O_2$ , contains two ethylenic linkings (Fokin, A., 1907, i, 10), and the author has effected oxidation with concentrated permanganate solution, obtaining valeric and azelaic acids, these two products accounting for fourteen of the carbon atoms in the chain. Further oxidation experiments with subsequent weighing of the carbon dioxide evolved showed that the remaining carbon was completely oxidised. Ozonisation of the acid confirmed this result, the products being 75% of the theoretical yield of azelaic acid, 50% of that of valeric acid, and a small quantity of succinic acid. The formula of elaeostearic acid is therefore  $CH_3(CH_2)_3CH:CH(CH_2)_2CH:CH(CH_2)_7CO_2H$ .

H. J. E.

**The Labile Nature of the Halogen Atom in Organic Compounds. VIII. The Action of Hydrazine on the Halogen Derivatives of Acetoacetic and Benzoylacetate Esters and of Benzoylacetone.** ALEXANDER KILLEN MACBETH (T., 1923, 123, 122—1130).

**Chlorine Derivatives of Pyruvic Acid.** EFIM FILIMOVITSCH KLIMENKO (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 290—293).—In view of the statement made by Seissl (A., 1889, 489), that the ester obtained by Klimenko (*Ber.*, 1870, 3, 465) from the product of the reaction between phosphorus pentachloride and pyruvic acid is not ethyl dichloropropionate but a mixture of the ethyl esters of monochloro- and dichloro-pyruvic acids, the latter acid is synthesised by the chlorination of pyruvic acid. *Ethyl dichloropyruvate* boils at 160—190°, whereas the ethyl dichloropropionate previously obtained is a crystalline solid, m. p. 115°. Seissl's views must therefore be considered to be incorrect.

R. T.

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**The Conversion of Malonic Acid into *d*-Malic Acid.** ALEX. MCKENZIE and HAROLD JAMES PLENDERLEITH (T., 1923, 123, 1090—1096).

**Ring-chain Tautomerism. V. The Effect of the gem-Dipropyl Grouping on the Carbon Tetrahedral Angle.** LESLIE BAINS and JOCELYN FIELD THORPE (T., 1923, 123, 1206—1214).

**Physical Properties of Maleic, Fumaric, and Malic Acids.** JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Amer. Chem. Soc.*, 1923, 45, 1003—1008).—Maleic anhydride has m. p. 52.6°; *i*-malic acid, m. p. 128.5—129°; maleic acid, m. p. 130—135°; fumaric acid, m. p. 284°; the solubility of these compounds in various common solvents has been determined and compared with previously recorded values. It is also shown that *i*-malic acid is less hygroscopic than citric and tartaric acids. The specific gravity of solutions of *i*-malic and maleic acids of various concentrations is shown graphically. W. S. N.

**Chromium Malate and Chromomalic Acid.** J. BARLOT and PANAITOPOL (*Bull. Soc. chim.*, 1923, [iv], 33, 306—311).—Chromium malate was obtained in less than 10% yield by dissolving chromium hydroxide in an aqueous solution of malic acid by the aid of heat, evaporating the solution, and purifying the product by successive precipitations from aqueous solution by means of acetone. To obtain an analytically pure product, the chromium hydroxide must be washed free from sodium, and the malic acid purified from potassium by precipitation of the latter as chloroplatinate. Quantitative yields were obtained by the action of a metallic malate on a solution of a chromium salt, and the best results from the point of view of isolating the product were given by acting on a solution of purified chromium sulphate with lead malate at 100°, filtering off the lead sulphate, removing the excess of lead in solution by treatment with hydrogen sulphide, and precipitating the chromium malate as small, anhydrous, greyish-green, hygroscopic crystals by addition of acetone. The anhydrous salt is soluble only with difficulty in water, but on evaporation of the solution a green, amorphous substance is obtained readily soluble in cold water. This is a hydrated substance of the composition  $2[(C_4H_4O_5)_3Cr_2] \cdot 13H_2O$ , which has acidic properties corresponding with the replacement of 5H, and salts are formed with metals, for example with lead, having the composition  $Pb_5[(C_4H_4O_5)_6Cr_4(OH)_5 \cdot 8H_2O]_2$ . These salts in analogy to the chromi-oxalates are termed chromimalates. From the green hydrated chromium malate, and from the chromimalates chromium is not precipitated by the usual reagents. G. F. M.

**Oxidation of Lignin Alcohol to Lignic Acid and the Occurrence of Lignic Acid.** J. GRÜSS (*Ber. Deut. bot. Ges.*, 1923, 41, 53—58; cf. this vol., i, 541).—The oxidation of lignin alcohol by means of hydrogen peroxide leads to *lignic acid*, isolated as the more soluble  $\alpha$ -copper salt,  $C_7H_{14}O_5Cu \cdot 5H_2O$ , and the less soluble  $\beta$ -copper salt. The former has been isolated from oak-wood attacked

by *Polyporus versicolor*, and from pine-wood attacked by *Trametes radiciperda*. A third copper salt has also been obtained from *mykolignic acid*, which is found in pine-wood infested by fungus; this acid gives *oxymykolignic acid* on oxidation by means of hydrogen peroxide. The copper salts are described in detail. W. S. N.

**Synthesis of Anemoninic Acid.** ATUSI FUJITA (*J. Pharm. Soc. Japan*, 1923, No. 492, 67—75).—Anemoninic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , has been synthesised from  $\delta$ -furylidenelevulic acid by Baeyer's method. The  $\delta$ -acid (10 g.), prepared by a somewhat modified method of Kehrer and Hofacker (A., 1897, i, 204), was dissolved in excess of sodium carbonate solution and reduced with 3% sodium amalgam (about 100 g.) to  $\delta$ -furfuryllevulic acid, white plates, m. p. 99°, the semicarbazone of which forms small white plates, m. p. 125°.  $\delta$ -Furfuryllevulic acid (4 g.) was dissolved in warm water (400 c.c.), to which bromine water (3.3 g. bromine) was added at a time. Then the mixture was mixed with moist silver oxide, prepared from 20.5 g. of silver nitrate, and warmed at 70° during three hours. After cooling, it was acidified with dilute hydrochloric acid, concentrated in a vacuum and extracted ten times with acetic ester, from which  $\alpha$ -anemoninic acid was obtained as a syrup containing some crystals. By treating with a small quantity of hydrochloric acid (20%), it was changed into the  $\beta$ -isomeride, colourless plates, m. p. 189°. K. K.

**Action of Molybdic Acid on the Rotatory Power of Tartaric and Malic Esters.** E. DARMOIS (*Compt. rend.*, 1923, 176, 1140—1142).—It has already been shown that molybdic acid causes a change in the rotatory power of tartaric and malic acids, and the subject was further investigated by studying the effect of molybdic acid in methyl and ethyl tartrates and malates in dilute aqueous solution. A progressive change in rotation occurred, the rate of which was greatly accelerated by an increase in temperature, but the final value attained was unaffected, as was also the dispersion. The rate of change in rotation and also the final value were dependent on the relative proportions of molybdic acid and ester. The addition of potassium hydroxide in amount less than one-fourth of the quantity required to form  $\text{K}_2\text{MoO}_4$  has no effect on the rate of variation of  $\alpha$ , but larger amounts cause a rapid acceleration of the change. Ammonium molybdate has a similar effect. With ethyl malate molybdic acid causes practically no change in rotation in the cold, but at 100° the change is rapid. It is concluded that the mutarotation is not due to a progressive esterification of the hydroxyl groups, but rather to a saponification of the esters.

G. F. M.

**Alkaline Hydrolysis of the Stereoisomeric Dimethyl Tartrates.** ANTON SKRABAL and LUDWIG HERMANN (*Monatsh.*, 1923, 43, 633—643).—A study of the relative rates of hydrolysis of methyl *d*- and *l*-tartrates, racemate, and *mesotartrate*, by sodium carbonate and by carbonate-hydrogen carbonate mixtures. An improved method for preparing the *d*-ester is described (cf.

Anschütz and Pictet, A., 1880, 876). It is shown that the two-stage hydrolysis of the *d*- and *l*-esters proceeds at the same rate, the ratio of the velocity constants,  $k_1$  and  $k_2$ , for the two stages, depending on the concentration of ester, being smaller if the ester concentration is increased. For 0.05 to 0.1 molar solutions of *d*-ester, at 25°,  $k_1=4.2 \times 10^{-2}$  and  $k_2=0.30 \times 10^{-2}$ ; for 0.005 to 0.01 molar solutions,  $k_1=6.06 \times 10^{-2}$  and  $k_2=0.31 \times 10^{-2}$ . Almost identical values for  $k_1$  and  $k_2$  were obtained for similar solutions of the *l*- and the *dl*-ester, whilst the *meso*-ester (0.01–0.005 molar) gave  $k_1=4.3 \times 10^{-2}$  and  $k_2=0.15 \times 10^{-2}$  (cf. A., 1920, ii, 239). E. E. T.

**Alkaline Hydrolysis of Diacetyl-*d*-tartaric [Diacetoxysuccinic] Acid and of its Methyl Ester.** ANTON SKRABAL and LUDWIG MEHR (*Monatsh.*, 1923, 43, 645–653).—The velocity of alkaline hydrolysis of diacetyl-*d*-tartaric acid and of its methyl ester have been investigated. In the case of the ester, the methyl groups hydrolyse more rapidly than the acetyl groups. In the two-stage hydrolysis of the methyl groups, the ratio of the velocity constants for the two stages is roughly 2:1. In the two-stage hydrolysis of the acetyl groups in the acid, the corresponding ratio is 3.5:1. E. E. T.

**Optical Rotation of Arabinic Acid and of the Alkali Arabinates.** MOISEI ABRAMOVITSCH RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 247–250).—Gum arabic is shown to contain potassium, magnesium, and calcium, and has  $[\alpha]_D -24.8^\circ$ . Pure arabinic acid prepared from this has  $[\alpha]_D -27.86^\circ$ , and not, as Scheibler states,  $-98.5^\circ$ . The lithium, ammonium, sodium, and potassium salts have  $[\alpha]_D -17.81^\circ$ ,  $-19.81^\circ$ ,  $-21.67^\circ$ , and  $-23.06^\circ$ , respectively,  $[\alpha]_D$ , as in previous cases, increasing with the atomic weight of the substituting metal. R. T.

***n*- $\alpha$ -Sulphobutyric Acid and its Optically Active Components.** H. J. BÄCKER and J. H. DE BOER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 79–82).—*n*- $\alpha$ -Sulphobutyric acid can be obtained by the action of ammonium sulphite on  $\alpha$ -bromobutyric acid and by sulphonation of ethylmalonic acid, but is best prepared by sulphonation of *n*-butyric acid with sulphur trioxide. The butyrylsulphuric acid formed in the cold changes into sulphobutyric acid on heating. The acid crystallises after a long time in a vacuum over phosphoric oxide in hard, very hygroscopic crystals, m. p.  $66^\circ$ , containing  $1\text{H}_2\text{O}$ . Aniline sulphobutyrate forms small, glistening plates, m. p.  $175^\circ$ , and the *p*-toluidine salt has m. p.  $163^\circ$ . When these salts are heated with an excess of the amine, the amide of the carboxylic acid is formed. Aniline butyranilide- $\alpha$ -sulphonate crystallises in concentrically grouped, feather-like needles, m. p.  $253$ – $256^\circ$ ; *p*-toluidine butyro-*p*-toluidide- $\alpha$ -sulphonate has m. p.  $260$ – $263^\circ$ , the corresponding *p*-anisidine compound  $242^\circ$ , and the *p*-phenetidine compound  $264$ – $266^\circ$ . When heated with aromatic *o*-diamines, sulphobutyric acid forms derivatives of benzimidazole. Benzimidazole-2-propylsulphonic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \text{C} \text{---} \text{CHEt} \text{---} \text{SO}_3\text{H} \\ \diagdown \text{NH} \end{smallmatrix}$ , from *o*-phenylenediamine, and methyl-

benzimidazole-2-propylsulphonic acid,  $C_6H_5Me \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix} C \cdot CHEt \cdot SO_3H$ ,

from 3:4-diaminotoluene, are white, crystalline substances of low solubility and high m. p. with properties similar to those of taurine.

The resolution of  $\alpha$ -sulphobutyric acid was accomplished through the strychnine salt. *Strychnine d-sulphobutyrate* crystallises in small, glistening needles containing  $2H_2O$ . The d- and l-barium salts form long needles containing  $2\frac{1}{2}H_2O$ , whilst the r-salt forms small, glistening leaflets containing  $2H_2O$ . The direction of rotation of the barium salts is opposite to that of the free acids. The magnitude of rotation varies with the concentration. The molecular rotation of the barium salt for sodium light is  $32.2^\circ$  in a 24% and  $29.9^\circ$  in a 5% solution. The presence of barium chloride lowers the rotation.

E. H. R.

**The Second Dissociation Constant of Sulphoacetic and  $\alpha$ -Sulphopropionic Acids.** H. J. BACKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 83—87).—Using the values of the first dissociation constants of  $\alpha$ -sulphoacetic and  $\alpha$ -sulphopropionic acids previously determined (this vol., i, 88), the values of the second dissociation constants have now been determined from the hydrogen-ion concentrations, measured colorimetrically, of the acid salts and of mixtures of the acid and neutral salts. The values found, which can only be regarded as approximations, are, at the ordinary temperature,  $\alpha$ -sulphoacetic acid,  $7.2$  to  $9.7 \times 10^{-5}$ ;  $\alpha$ -sulphopropionic acid,  $4.2$  to  $6.0 \times 10^{-5}$ . E. H. R.

**Viscosity of the Systems Water-Bromal and Chloral-Dimethylethylcarbinol.** NIKOLAI NIKOLAEVITCH EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 338—371).—Binary fusion, viscosity, and density diagrams are constructed for the systems bromal-water and chloral-dimethylethylcarbinol. For the former system, maxima exist in the fusion and viscosity diagrams at 50 mol. %, corresponding with the formation of bromal hydrate. The summit of the viscosity isotherms moves from 50 to 42.5 mol. % on changing the temperature from  $40^\circ$  to  $100^\circ$ , and a similar change occurs in the isotherms of the temperature coefficients of viscosity, indicating that some dissociation of the compound occurs at higher temperatures. The minimum boiling-point mixture contains 35—45 mol. % of bromal. Bromal hydrate and its mixtures with bromal or water readily lose water with rise of temperature, causing the separation of the liquid into two layers. The density curves for both the system and chloral-dimethylethylcarbinol exhibit at first a rapid and then a gradual rise up to 100% of the halogen compounds. The viscosity isotherms and temperature coefficient of viscosity curves of the latter system are similar in type to those of the former, and indicate the formation of an equimolecular compound similar in properties to chloral hydrate or ethylate.

R. T.

**Trimethylacetaldehyde** [ $\alpha\alpha$ -Dimethylpropaldehyde]. I. ADOLF FRANKE and HERMANN HINTERBERGER (*Monatsh.*, 1923, 43, 655—660).—The aldehyde is prepared as follows: *iso*Butyl

alcohol is passed, together with carbon dioxide, through a brass tube filled with brass turnings and heated at 500—550°, when it is converted into isobutyraldehyde. The latter is converted into  $\beta\beta$ -dimethylpropan- $\alpha\gamma$ -diol, from which  $\beta\beta$ -dimethylpropyl alcohol is prepared as previously described (A., 1914, i, 7), although better conditions are now detailed. By passing the vapours of the last-named alcohol through a hot tube (as before),  $\alpha\alpha$ -dimethylpropaldehyde was obtained, and has been studied from the point of view of its possible resemblance to benzaldehyde rather than to a typical aliphatic aldehyde.

When treated with a little concentrated sulphuric acid, it rapidly polymerises to give a trimeride (needles, m. p. 82°) which is distinct from a similar compound described by Richard (A., 1911, i, 6). When heated in alcoholic solution with potassium cyanide, the aldehyde gives a small quantity of an acid (needles, m. p. 223°), presumably of the benzilic acid type, and formed as a result of the alkaline properties of potassium cyanide. E. E. T.

**The Isomeric Trithioacetaldehydes.** FREDERICK GEORGE MANN and (SIR) WILLIAM JACKSON POPE (T., 1923, 123, 1178—1181).

**Preparation of the Homologues of Mesityl Oxide by the Action of Gaseous Hydrogen Chloride on Ketones.** C. V. GHEORGHIU (*Bull. Acad. Sci. Roumaine*, 1923, 8, 68—71).—An attempt to condense homologues of acetone yielded, in the case of a mixture of acetone with methyl ethyl ketone, mesityl oxide, methylmesityl oxide with a larger amount of  $\beta\gamma$ -dimethyl- $\Delta^2$ -pentene- $\delta$ -one and small quantities of  $\gamma$ -methyl- $\Delta^2$ -hexene- $\epsilon$ -one and  $\gamma\delta$ -dimethyl- $\Delta^2$ -hexene- $\epsilon$ -one. From methyl ethyl ketone,  $\gamma\delta$ -dimethyl- $\Delta^2$ -hexene- $\epsilon$ -one is the chief product. The yield in both cases is small owing to resinification. H. J. E.

**Syntheses of  $\alpha$ -Diketones by Means of Organo-zinc Derivatives.** E. E. BLAISE (*Compt. rend.*, 1923, 176, 1148—1150; cf. this vol., i, 181).—It has been shown previously that the condensation of zinc propyl iodide with oxalylbisoxymethyl chloride gives a mixture of the bisoxycycloacetatoxyisobutyrylates of propylglyoxal and of dibutyryl. After alcoholysis of the mixed products only the latter remains. This forms a crystalline substance, m. p. 55—80°, consisting of a mixture of the internally compensated and the racemic isomerides. They could only be separated by slow crystallisation from methyl alcohol, and mechanical separation of the two kinds of crystals formed. The pure substances melt at 72° and 82°, respectively, and boil at 168°/13 mm. Hydrolysis of the mixed isomerides by means of hydriodic acid was accompanied by reduction, and propyl *n*-butyl ketone was formed, b. p. 163°, giving a semicarbazone, m. p. 96°. Hydrolysis by means of a mixture of hydrochloric and acetic acids gave, however, dibutyryl in 60% yield. It is a yellow liquid, b. p. 61.5°/14 mm. The dioxime melts at 181—182°, and the disemicarbazone above 250°.

G. F. M.

**The Oxidation of Dextrose by Yellow Oxide of Mercury, and the Preparation of Gluconic Acid.** A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1923, [iv], 33, 345–348).—Gluconic acid was obtained as its calcium salt in almost theoretical yield by the oxidation of a 10% solution of dextrose with yellow mercuric oxide in presence of calcium carbonate. After boiling for twenty-four hours, the liquid was filtered from the mercurous oxide and mercury formed, concentrated by evaporation on a water-bath, and mercury precipitation of the calcium salt induced by the addition of an excess of alcohol. The pasty mass which separates becomes crystalline on keeping for several days over sulphuric acid. It was further purified by recrystallisation from water and alcohol. It contains 1 mol. of water, which it retains somewhat tenaciously, desiccation at 70–80° in a vacuum being necessary for the production of the anhydrous salt.

G. F. M.

**Carbohydrate Sulphates. VI. Acetone [isoPropylidene] Compounds of Dextrose Sulphates.** HEINZ OHLE (*Biochem. Z.*, 1923, 136, 428–448; cf. A., 1922, i, 986, this vol., i, 441).—Purified diisopropylidenedextrose, treated in pyridine solution with chlorosulphonic acid in chloroform, yields the crystalline pyridine salt of diisopropylidene-dextrose sulphate; it has m. p. 163–164° and  $[\alpha]_D^{20}$  –21.9° in chloroform ( $c=2.9$ ). The sodium salt has  $[\alpha]_D^{20}$  –14.7° in water ( $c=3.27$ ). It forms a crystalline additive product with sodium acetate, having  $[\alpha]_D^{20}$  –13.4° and decomposing at 221–222°. The brucine salt melts at 248° and has  $[\alpha]_D^{20}$  –27.6° in water and –30.98° in chloroform. When recrystallised from alcohol, pyridine diisopropylidene-dextrose sulphate loses one molecule of acetone and yields pyridine isopropylidene-dextrose  $\gamma$ -sulphate, m. p. 134°,  $[\alpha]_D^{20}$  –13.5° in water. The sodium salt is amorphous and hygroscopic, but the barium salt crystallises with 5 molecules of alcohol and has  $[\alpha]_D^{20}$  –14° in water. On boiling an alcoholic solution of the pyridine salt for four hours, the sulphuric acid is removed quantitatively as ethylsulphuric acid, identified as its brucine salt, m. p. 200–201°,  $[\alpha]_D^{20}$  –29.7° in water, and crystallising with 3/4 mol. of alcohol. isoPropylidene-dextrose  $\gamma$ -sulphuric acid is reconverted into the diisopropylidene-dextrose by shaking the pyridine salt with an equal weight of copper sulphate in fifty volumes of acetone for thirty-six hours. isoPropylidene-dextrose-6-sulphuric acid, which was isolated either as its crystalline sodium salt, m. p. 157°,  $[\alpha]_D^{20}$  –9.88°, crystallising with  $\frac{1}{2}$  H<sub>2</sub>O, as its amorphous barium salt,  $[\alpha]_D^{20}$  –7.2° in water, or better as its crystalline strychnine salt, m. p. 178–182° (when dried), and N/10-sulphuric acid solution, it loses acetone and yields dextrose-6-sulphuric acid, identifiable as its brucine salt and identical with Soda's preparation (this vol., i, 441). Strychnine-dextrose-6-sulphate monohydrate crystallises well, but during crystallisation its initial rotation falls from –6.27° to –3.12°, whilst its final value remains at –0.7°. A discussion follows of the mechanism of combination

of acetone with dextrose. Evidence has been obtained of intermediate combination with hydrochloric and with sulphuric acids.

H. K.

**Extraction of  $\beta$ -Ethylgalactoside in the Presence of a Large Proportion of Reducing Sugars.** J. CHARPENTIER (*J. Pharm. Chim.*, 1923, [vii], 27, 368—371).—Galactose has been identified in the products of the hydrolysis of gum arabic by converting it into  $\beta$ -ethylgalactoside by means of emulsin (cf. Bourquelot and Bridel, A., 1920, i, 530). All attempts to extract the  $\beta$ -ethylgalactoside with ethyl acetate gave a product which was contaminated with a large proportion of arabinose. By the action of hydrocyanic acid, however, in the presence of a trace of ammonia the sugar is converted into a nitrile which is hydrolysed to the acid containing one atom of carbon more than the original sugar. This acid is completely precipitated by basic lead acetate, and the  $\beta$ -ethylgalactoside is recovered from the filtered solution. It was obtained as somewhat voluminous, transparent crystals, melting at 159—160° and giving  $[\alpha]_D -4.40^\circ$ .

W. T. K. B.

**The Acetone [isoPropylidene] Compounds of Xylose.** OLOF SVANBERG and KNUT SJÖBERG (*Ber.*, 1923, 56, [B], 863—869).—In a recent communication (Freudenberg and Svanberg, A., 1922, i, 1116), the preparation of diisopropylidene-xylose by the action of hydrogen chloride on a suspension of xylose in acetone has been described. The remarkable observations were made that a portion of the catalyst appears to pass into a non-ionised form (and to be lost subsequently during the distillation in a high vacuum) and that the diisopropylidene-xylose is very pronouncedly mutarotatory. The behaviour of the hydrogen chloride, however, is shown to be independent of the presence of xylose and to be due in all probability to the formation of an additive product with mesityl oxide or phorone; this is not very material in the cases of the preparation of crystalline isopropylidene sugars, but if, as in the present instance, the products must be purified by distillation, it may easily happen that the distillates are contaminated with hydrogen chloride. Actually, the observed mutarotation of the specimens of diisopropylidene-xylose is shown to be due to this cause and the consequent hydrolysis of the substance to mono-isopropylidene-xylose.

Pure diisopropylidene-xylose, b. p. 85—87°/0.5 mm.,  $[\alpha]_D^{25} +14.0^\circ$  (constant), is conveniently prepared in 80% yield by agitating xylose with a solution of concentrated sulphuric acid in acetone at the atmospheric temperature and subsequent neutralisation of the mixture with barium and calcium carbonates. The rapidity with which the sugar dissolves depends greatly on the purity and dryness of the solvent. The residues from the preparation of the diisopropylidene compound contain small amounts of mono-isopropylidene-xylose, colourless needles, m. p. 41—43°,  $[\alpha]_D^{25} -19.0^\circ$  in aqueous solution (2—4%). The latter compound is more conveniently prepared by the partial hydrolysis of diisopropylidene-xylose by very dilute hydrochloric acid at 18°, the course of the

change, which is unimolecular, being conveniently followed by polarimetric observation.

H. W.

**The Structure of Sucrose.** MAX BERGMANN (T., 1923, 123, 1277—1279).

**Investigation of the Mannan Present in Vegetable Ivory.** JOCELYN PATTERSON (T., 1923, 123, 1139—1149).

**Cellulose Xanthates.** R. WOLFFENSTEIN and E. OESER (*Ber.*, 1923, 56, [B], 785—787).—The action of sodium hydroxide solution (d 1.2) and carbon disulphide on different cellulose acetates which are soluble in acetone leads to the formation of a *cellulose xanthate*,  $C_6H_5(O\text{Na})_2(O\text{-C}\cdot\text{S}\cdot\text{SNa})_2$ , which, in contrast to the product derived from cellulose, appears to be derived from a parent substance containing five active hydroxyl groups. It is a dark brown, resinous material which more readily evolves carbon disulphide on exposure to moist air than does the sodium salt of the more usual cellulose xanthate. It gives salts with the heavy metals which are less stable than the corresponding compounds from alkali-cellulose.

H. W.

**"Hydrocellulose." A Summary of the Literature.** PERCY HERBERT CLIFFORD (*J. Text. Inst.*, 1923, 14, T.69—77).—A review of the literature dealing with the preparation and properties of "hydrocellulose." Seventy-one references are cited.

J. C. W.

**Polysaccharides. \*VIII. Lichenin.** P. KARRER and B. JOOS (*Biochem. Z.*, 1923, 136, 537—541).—Lichenin from *Cetraria islandica* is closely allied to cellulose. By acetolysis at 120°, it yields octa-acetylcellobiose, and with acetyl bromide at 40° yields acetobromocellobiose. Lichenin acetate is prepared like cellulose acetate, and has a similar rotation,  $[\alpha]_D^{20} -23.8^\circ$  (in chloroform + methyl alcohol, 9:1). It yields aceto-1:6-dibromoglucose on treatment with phosphorus pentabromide. Lichenin is soluble in dilute alkali and in hot water.

H. K.

**Lignin.** J. GRÜSS (*Ber. Deut. bot. Ges.*, 1923, 41, 48—52; cf. Klasen, A., 1920, i, 821; 1922, i, 324; Beckmann, Liesche, and Lehmann, A., 1921, i, 546; 1922, i, 233; Paschke, A., 1921, i, 772; 1922, i, 325).—The action of ethyl-alcoholic hydrogen chloride on wood, previously extracted by means of 4% sodium hydroxide solution and boiling water, gives a substance described as *lignin alcohol*,  $C_{28}H_{46}O_{10}$ , m. p. 160°, *vanadium* derivative,  $C_{28}H_{42}O_{10}V_2$ , a microcrystalline powder. Numerous colour reactions of lignin alcohol are described (cf. Crocker, A., 1921, , 839).

W. S. N.

**Lignin.** EMIL HEUSER and ARNE WINSVOLD (*Ber.*, 1923, 56, B], 902—909).—Lignin has been considered to be an aromatic compound, whilst, on the other hand, arguments have been advanced in favour of an aliphatic structure, such as that of the cellulose and pentosans of wood. In the authors' opinion, the chemical evidence available is insufficient at the present to enable a definite decision

between these alternatives to be made, but in the present communication a number of experiments are quoted the results of which point to the conclusion that the molecule of lignin contains a benzenoid nucleus with oxidisable side chains.

Treatment of lignin with molten potassium hydroxide has been shown previously to lead to the formation of protocatechuic acid, pyrocatechol, and oxalic acid, whereas cellulose under similar conditions gives large amounts of oxalic acid and small quantities of protocatechuic acid and pyrocatechol. The previous results may be summarised in the statement that lignin and cellulose behave differently towards molten potassium hydroxide, the former giving mainly aromatic compounds, the latter chiefly oxalic acid. If the treatment of lignin is effected in an atmosphere of hydrogen or nitrogen the production of oxalic acid is very greatly diminished whereas that of aromatic compounds, particularly pyrocatechol, considerably increased. The formation of pyrocatechol from lignin is doubtless a secondary change due to the further decomposition of protocatechuic acid primarily formed. The latter substance by itself requires a high temperature ( $360^{\circ}$ ) to effect the complete removal of carbon dioxide, but in the presence of potassium hydroxide the change occurs at  $240^{\circ}$ . If air is present, the yield of pyrocatechol is small (1–3%), but oxalic acid is formed in considerable quantity (14–16%). The displacement of the yields in favour of pyrocatechol can also be greatly influenced by the presence of iron, which doubtless acts catalytically. Protocatechuic and oxalic acids are not present in the product, so that the decomposition of the former is also accelerated by the catalyst. Actually, a part of the pyrocatechol which is produced also suffers further change under these conditions, since the yield of the substance is only 23% of the weight of lignin taken.

Protocatechuic acid is converted by molten potassium hydroxide at  $240$ – $280^{\circ}$  in the presence of air into pyrocatechol (2.5%) and oxalic acid (about 20%), whilst 70% of it remains unchanged. In an atmosphere of hydrogen, the yields are pyrocatechol (19%), oxalic acid (0%), unchanged protocatechuic acid (77%), whilst in the presence of iron and hydrogen they are pyrocatechol (26%) and unchanged protocatechuic acid (0%).

The behaviour of ligninsulphonic acid towards molten potassium hydroxide is generally similar to that of lignin prepared by Willstätter's method.

The communication concludes with an extended, adverse criticism of the method proposed by Schmidt (A., 1921, i, 912; 1922, i, 206; this vol., i, 274) for the estimation of lignin in wood (the results of which are not in harmony with those obtained by the customary methods) and of the introduction of the conception of "skeleton substance."  
H. W.

**Humic Acids. IV. Preparation and Properties of Artificial and Natural Humic Acids.** WILHELM ELLER (and, in part, H. SAENGER, K. WENZEL, H. SEILER, and H. PIEPER) [*Annalen*, 1923, 431, 133–161].—An extension of previous work on the

subject (A., 1920, i, 733). Phenols are oxidised in alkaline solution by exposure to the air, by addition of hydrogen peroxide, by addition of potassium persulphate, or by electrolysis. In respect to the humic acids to which they give rise, the phenols investigated fall into four classes. (1) Hydroxyquinol gives a humic acid,  $(C_7H_5O_3)_x$ , which is also produced from hydroxyquinol triacetate; methylquinol is converted into the homologue,  $(C_7H_5O_3)_x$ . (2) Pyrogallol is oxidised to a humic acid,  $(C_{10}H_7O_{11})_x$ ; if insufficient alkali or persulphate is used, purpurogallin and a *hexahydroxydiphenyl*, m. p.  $230^\circ$ , are formed, either of which gives the same humic acid on continued oxidation. It is not, however, possible to obtain a pure humic acid by the oxidation of phloroglucinol, its triacetate, its diethyl ether, or its carboxylic acid. (3) Salicylic acid, gentisic acid, and 2:4:2':4'-tetrahydroxydiphenyl, in contrast to the phenols of the previous classes, undergo oxidation with elimination of carbon dioxide and production of a humic acid containing 56.37–56.57% carbon, 2.49–2.58% hydrogen, for which no formula has yet been devised. (4) The oxidation of phenol, *o*-cresol, resorcinol, or 3:5:3':5'-tetrahydroxydiphenyl leads to a product of variable composition. Nevertheless, it is shown that the properties (*loc. cit.*) of any of these phenol-humic acids are the same as those of the natural humic acids.

It is known that humic acids decompose at  $80^\circ$  (A., 1921, i, 506); this is doubtless the reason why humic acids prepared from carbohydrates by previous workers vary in composition. Indeed, it is now shown that if the temperature of reaction does not exceed  $70^\circ$ , the action of 45–50% aqueous sulphuric acid on sucrose, lactose, or dextrose leads to the formation of a humic acid,  $(C_7H_5O_3)_x$  (cf. Bottomley, A., 1915, i, 648), the composition of which is constant. A homogeneous product is not, however, obtained by the action of sulphuric acid on cellulose. Humic acids from carbohydrates show slight differences in their solubility, when compared with natural humic acids or those derived from phenol. Moreover, both natural and phenol-humic acids absorb atmospheric oxygen when moistened with alkali hydroxide solution; when they are warmed to about  $100^\circ$  with phenylhydrazine carbamate, nitrogen is evolved. These reactions are not, however, given by humic acids derived from carbohydrates (cf. following abstract).

W. S. N.

#### Humic Acids. V. Action of Nitric Acid on Humic Acids.

WILHELM ELLER, HARRY MEYER, and HANS SAENGER (*Annalen*, 1923, 431, 162–177; cf. preceding abstract).—The similarity between the natural humic acids and those derived from phenols is shown to extend to their derivatives. The action of cold concentrated nitric acid on quinol-humic acid gives *seminitrohumic acid*,  $(C_{12}H_7O_8NO_2)_x$ , a brownish-red, amorphous, hygroscopic powder, which is soluble in water, but tends to form colloidal solutions; the aqueous solution has an acid reaction, but does not decompose alkali carbonates. A product identical in composition and properties is obtained by the action of cold concentrated nitric

acid on natural humic acid; the insoluble material formed in this reaction is held to be an adsorption-compound of the nitro-acid and inorganic salts. Seminitrohumic acid causes the elimination of nitrogen when warmed with phenylhydrazine carbamate at 70°; its aqueous solution gives an intense red coloration when warmed with potassium cyanide solution. The action of hot, concentrated nitric acid leads to the formation of oxalic acid, carbon dioxide, and hydrogen cyanide.

When quinol-humic acid is treated with boiling concentrated nitric acid, oxidation and nitration occur simultaneously, with formation of a yellow, amorphous, very hygroscopic powder, *nitrohydroxyhumic acid*, the composition of which varies. In contrast to nitrohumic acid, it is insoluble in alcohol.

When quinone is treated with boiling concentrated nitric acid, nitration and polymerisation both occur, the product, *nitroquinone-humic acid*, being a reddish-yellow, amorphous, hygroscopic powder the composition and properties of which are intermediate between those of nitrohumic acid and nitrohydroxyhumic acid. When it is heated with phenylhydrazine carbamate, nitrogen is evolved at 80°. It forms a colloidal aqueous suspension.

The product of the action of cold concentrated nitric acid on sucrose-humic acid is a faintly yellowish-brown, amorphous powder,  $(C_{21}H_{21}O_{14}N_2)_2$ , which is only stable to air and sunlight after drying; it is soluble in alkalis or ammonia, and in water, alcohol, or acetone when freshly prepared, or on warming. In contrast to the other humic acids described, it decolorises aqueous potassium permanganate solution.

W. S. N.

**Humic Acids. VI. Action of Chlorine on Humic Acids.** WILHELM ELLER, ERNST HERDIECKERHOFF, and HANS SAENGER (*Annalen*, 1923, **431**, 177—186).—The action of chlorine gas at 50—70°, in the absence of air and sunlight, on an aqueous suspension of quinol-humic acid gives a golden-yellow, infusible, amorphous powder, *chlorohumic acid*,  $C_{10}H_5O_6Cl_5$ , which, when heated, decomposes below 100°, more rapidly at higher temperatures. When chlorohumic acid is heated with phenylhydrazine carbamate, nitrogen is evolved at 70°. Since it forms true solutions in ether, phenol, or glacial acetic acid, the molecular weight can be determined; in the formation of chlorohumic acid it is suggested that the six-membered rings in humic acid (A., 1921, i, 506) become converted into five-membered rings. The action of chlorine under the same conditions on natural humic acid gives identically the same product, but from sucrose-humic acid a pale-yellow, amorphous powder, decomp. 150°  $(C_{21}H_{21}O_{13}Cl_4)_2$ , is produced the properties of which are compared with those of the other humic acids as follows. The chloro-derivative from sucrose-humic acid is incompletely soluble in alcohol, and insoluble in ether, phenol, or acetic acid; the chloro-acids from phenols or natural acids very readily form true solutions in these solvents. The chloro-acid from sucrose, is stable to boiling water; the other chloro-acids are immediately decomposed with elimination of carbon dioxide. The chloro-acids

from natural or phenol-humic acids are immediately decomposed by means of cold concentrated alkali hydroxide solution, whereas the acid derived from sucrose is stable.

W. S. N.

**Conversion of Alanine into Pyruvic Acid by the Direct Action of Oxygen.** L. J. SIMON and LÉON PIAUX (*Compt. rend.*, 1923, 176, 1227—1229).—Whilst oxidising agents convert alanine into acetaldehyde, carbon dioxide, and ammonia, the direct action of oxygen itself on a solution of the sodium salt in presence of small amounts of copper causes the formation of pyruvic acid to the extent of a maximum of about 8%, when 0.25 atom of copper is present for each molecule of alanine. With greater proportions of copper, the amount of pyruvic acid produced progressively decreases, and as this decrease is not due to the further oxidation of pyruvic acid, it is clear that two quite distinct reactions are involved, one giving rise to pyruvic acid, and the other to acetaldehyde. These results lend support to the suggestion of Neubauer and Fromherz that pyruvic acid is an intermediate product in the biochemical transformation of amino-acids into alcohols.

G. F. M.

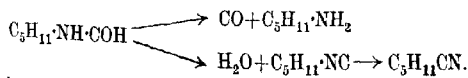
**The Optical Activity of Leucine and its Salts with Alkali Metals.** M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 32—93).—The molecular rotation of leucine salts is higher than that of the parent acid, and increases with the atomic weight of the metal. Thus  $[\alpha]_D$  for leucine in aqueous solution is  $-3.39^\circ$ ; lithium salt,  $-8.35^\circ$ ; ammonium salt,  $-10.34^\circ$ ; sodium salt,  $-20.21^\circ$ ; potassium salt,  $-23.22^\circ$  (cf. this vol., i, 494).

G. A. R. K.

**Optical Rotation of L-Aspartic Acid and its Alkali Salts.** M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 245—247).—The specific rotation of aspartic acid is found to be  $[\alpha]_D +3.63^\circ$ , not, as stated,  $+4.36^\circ$ . The lithium, ammonium, sodium, and potassium salts have  $[\alpha]_D -4.86^\circ$ ,  $-7.60^\circ$ ,  $-9.09^\circ$ , and  $-14.20^\circ$ , respectively,  $[\alpha]_D$  increasing with the atomic weight of the substituting metal.

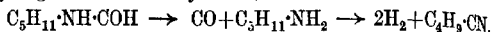
R. T.

**Decomposition of the Formamides of Aliphatic Amines.** A. MAILHE (*Compt. rend.*, 1923, 176, 1159—1161; cf. this vol., i, 458).—The catalysis of the formyl derivatives of aliphatic amines over alumina at  $400-410^\circ$  proceeds in the same way as that of the corresponding aromatic compounds, with the formation of the amine and liberation of carbon monoxide. At the same time, a certain amount of nitrile is formed due to the dehydration of the amine. Thus isoamylformamide gave a mixture of isoamylamine and isovaleronitrile:



Catalysis over nickel at  $360^\circ$  furnishes carbon monoxide and dioxide, hydrogen, methane, olefines, and an alkaline condensate, b. p.

120—130°, consisting mainly of *isobutyronitrile* produced by the dehydrogenation of *isoamylamine*,

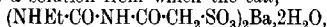


A portion of the *isoamylamine* is resolved into ammonia and *isoamylene*, which in its turn is decomposed further into methane, ethylene, etc. The hydrogenation of *isoamylformamide* over nickel at 200—210° gives a certain amount of secondary amine, *methylisoamylamine*, b. p. 108°, but the water produced hydrolyses some of the formamide to the primary amine, and the product is therefore a mixture of the two amines. G. F. M.

**Carbamide and Guanidine Derivatives of Aliphatic Sulphonic Acids.** RUDOLF ANDREASCH (*Monatsh.*, 1923, 43, 485—491).—A continuation of previous work (A., 1880, 877; 1883, 664). Sulphoacetylcarbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ , which cannot itself be obtained, forms well-defined salts. The potassium and ammonium salts are obtained by treating chloroacetylcarbamide with potassium and ammonium sulphite, respectively. If carbamide (10 g.), chloroacetic acid (16 g.), and phosphoryl chloride (15 g.) are heated together for three hours at 100°, a 75% yield of chloroacetylcarbamide results.

The potassium salt (needles, +1H<sub>2</sub>O) of *sulphoacetylmethylcarbamide*,  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ , is similarly obtained from chloroacetylmethylcarbamide (cf. Frerichs, A., 1899, i, 795, 796).

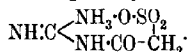
*Chloroacetylmethylcarbamide*, obtained from ethylcarbamide and chloroacetyl chloride, forms needles, m. p. 138°, and with potassium sulphite gives a solution from which the salt,



is obtained after evaporating in presence of barium acetate and extracting the potassium acetate with alcohol.

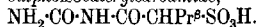
Potassium *sulphoacetylphenylcarbamide* is obtained from chloroacetylphenylcarbamide and potassium sulphite.

Chloroacetylguanidine hydrochloride, after treatment with potassium hydroxide and sulphite, yields *sulphoacetylguanidine*,



*s*-Diphenylcarbamide reacts slowly with chloroacetyl chloride to give a *chloroacetyl* derivative, m. p. 180°.

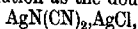
The successive actions of chloroacetyl chloride and ammonium sulphite on dicyanodiamidine sulphate give needles, m. p. 108°, probably the ammonium salt (+2H<sub>2</sub>O) of *sulphoacetyldicyanodiamidine*,  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ . Ammonium sulphite converts "bromural" (bromoisovalerylcarbamide) into the ammonium salt of *sulphoisovalerylcarbamide*,



*iso*Valerylcarbamide was isolated as well, but was probably present in the commercial bromural used. E. E. T.

**The Action of Potassium Cyanide on Monochloroamine.** W. F. SHORT (*Chem. News*, 1923, 26, 100—101).—A method is

described for the preparation of dicyanamide from a solution of hypochlorite and ammonia by the addition of potassium cyanide. It was removed from solution as the double silver salt,

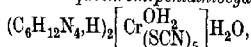


from which the dicyanamide hydrochloride could be recovered. Cold hydrochloric acid converted the silver compound into a cyanocarbamide,  $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{CN}$ . After precipitation of the silver by hydrogen sulphide, and concentration of the solution in a vacuum, an insoluble, amorphous polymeride of dicyanamide separated as a jelly-like mass.

W. E. G.

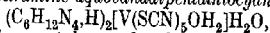
**Complex Thiocyanates of Tervalent Elements.** G. SCAGLIARINI and G. TARTARINI (*Gazzetta*, 1923, 53, i, 139—143).—The authors have successfully repeated Rosenheim and Cohn's attempts (A., 1901, i, 455) to prepare chromithiocyanates with the value of the ratio  $\text{Cr}:\text{SCN}$  other than 1:6, advantage being taken of Bjerrum's suggestion to effect the reactions in hot solutions containing an acid (A., 1922, i, 19). The hexathiocyanates of chromium are so stable that energetic chemical reagents are necessary to decompose them, and the chromithiocyanic acid from which they are derived is a resistant complex of pronounced acid character. Vanadium, iron, and aluminium form, however, less stable hexacid salts, which allow more readily of the gradual demolition of the complex anion. Thus a dilute solution of ammonium vanadithiocyanate contains at least a penta-aquo-salt, which may be rendered evident by conversion into the slightly soluble hexamethylenetetramine salt.

*Hexamethylenetetramine aquochromipentathiocyanate*,



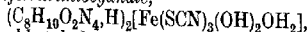
forms violet crystals, and *hexamethylenetetramine chromihexathiocyanate*,  $(\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H})_3[\text{Cr}(\text{SCN})_6]$ , pale violet crystals.

*Hexamethylenetetramine aquovanadipentathiocyanate*,



forms brick-red crystals and the *aquoferripentathiocyanate*,  $(\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H})_2[\text{Fe}(\text{SCN})_5\text{OH}_2]$ , dark green, almost black crystals.

*Caffeine aquoferritritthiocyanate*,



forms mosaic gold, tabular crystals.

T. H. P.

**The Catalytic Reduction of Aliphatic Azines. II. Reduction of Dimethylketazine and isoButyraldazine in the Presence of Glacial Acetic Acid.** K. A. TAIPALE (*Ber.*, 1923, 56, [B], 954—962).—It has been found by the author (the communication will be published later) that dimethylketazine can be hydrogenated in the presence of platinum black to the corresponding symmetrical secondary hydrazine, and that the method can be extended to other aliphatic ketazines and aldazines, giving thus a method for the preparation of the difficultly accessible aliphatic hydrazohydrocarbons. Reduction, however, occurs very slowly, and the yields do not exceed 60% of those theoretically possible. It is found in the case of dimethylketazine that these disadvantages

can be largely avoided if the reaction is effected in glacial acetic acid solution. Under definite conditions, the change occurs with sufficient rapidity, and the yield of hydrazine attains 90%. The corresponding primary and secondary amines are formed as by-products and, in contrast to the action with the ketazine alone or in the presence of a neutral solvent, ammonia is produced in small amount. As the quantity of acetic acid is increased, the yields of the hydrazine diminish.

With *isobutyraldazine* the process is not so successful. The rapidity of hydrogenation is increased, but the yield of the hydrazine is diminished, whereas that of amines and ammonia is increased. In this case, also, increasing amounts of by-products are formed as the dilution of the solution increases. On the other hand, undue concentration of the solution causes gradual cessation of the change owing to the separation of solid acetates. The difficulty is most readily avoided by operating in alcoholic or ethereal solution with addition of a quantity of acetic acid which is approximately equivalent to the azine used.

The following compounds call for mention. *Diisopropylhydrazine dihydrochloride*,  $\text{CHMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CHMe}_2\cdot 2\text{HCl}$ , and the corresponding monohydrochloride, m. p. 203–204° after softening at 200°, and *monoperchlorate*, m. p. 145–146°. *Diisopropylsemicarbazide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NPr}^i\cdot\text{NHPr}^i$ , m. p. 103–104°. *Monobenzoyldiisopropylhydrazine*,  $\text{NHPr}^i\cdot\text{NBzPr}^i$ , m. p. 44·5°. *Diisobutylhydrazine dihydrochloride*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHMe}_2\cdot 2\text{HCl}$ , and the corresponding monohydrochloride have m. p. 175° when heated rapidly. The *monoperchlorate*, m. p. 159° (decomp.), when rapidly heated, and the *dibenzoyl* derivative, small needles, m. p. 79–80°, are described. *Diisobutylsemicarbazide* crystallises in hexagonal plates, m. p. 132°.

*Diisobutylamine chloraurate* forms yellow crystals, decomp. 199–200°. H. W.

[No reference is made to the papers by Lochte, Bailey, and Noyes, A., 1922, i, 328; this vol., i, 26.]

**Bismuth Cacodylate.** P. CLAUSMANN (*Bull. Soc. chim.*, 1923, [iv], 33, 447–448).—A crystalline bismuth cacodylate of the composition  $(\text{AsMe}_2\text{O}_2)_3\text{Bi}\cdot 8\text{H}_2\text{O}$ , was obtained by dissolving the theoretical amount of bismuth oxide in a hot concentrated aqueous solution of cacodylic acid, filtering, and allowing the salt to crystallise. It forms colourless, hexagonal crystals, m. p. 82°. The whole of the water of crystallisation is not eliminated even at 120°, and above this temperature decomposition occurs. The salt is not so readily hydrolysed as the salts of bismuth with mineral acids. A similar compound cannot be obtained by double decomposition between a bismuth salt and an alkali cacodylate.

G. F. M.

**An Electrolytic Method for the Preparation of Mercury Dimethyl.** J. LEWIS MAYNARD and HENRY C. HOWARD, jun. (*T.*, 1923, 123, 960–964).

**Further Experiments on the Catalytic Dehydrogenation of Hexahydroaromatic Hydrocarbons.** N. ZELINSKY (*Ber.*, 1923, 56, [B], 787—788).—*o*-Dimethylcyclohexane is almost completely dehydrogenated to *o*-xylene when passed three times over platinum black at 300—310°; under similar conditions at 310°, *m*-dimethylcyclohexane yields *m*-xylene quantitatively. Four successive passages of *p*-dimethylcyclohexane over palladium black at 310° gives *p*-xylene in 96% yield, whereas menthane is largely transformed into *p*-cymene by two successive treatments at 300—305°. H. W.

**The Preparation of Aromatic Chloromethyl Derivatives.** G. BLANC (*Bull. Soc. chim.*, 1923, [iv], 33, 313—319).—Chloromethyl derivatives of aromatic hydrocarbons were obtained, in most cases in good yield, by the action of hydrogen chloride on trioxymethylene, or, more conveniently, 40% formaldehyde solution, and the hydrocarbon in presence of zinc chloride at about 60°. Thus from benzene an 80% yield of benzyl chloride together with *p*-dichloromethylbenzene were obtained. With larger quantities of zinc chloride and a more slowly conducted reaction, considerable amounts of diphenylmethane were obtained. From toluene, 1-methyl-4-chloromethylbenzene was prepared in a similar manner, whilst *m*-xylene gave 1:3-dimethyl-4-chloromethylbenzene, b. p. 115°/15 mm., and 1:3-dimethyl-4:6-dichloromethylbenzene, m. p. 93°. From ethylbenzene *p*-chloromethylethylbenzene was obtained, b. p. 95—96°/15 mm., and cumene gave a 75% yield of *p*-chloromethylisopropylbenzene, b. p. 100°/14 mm. Cymene was converted into 1-methyl-2-chloromethyl-4-isopropylbenzene, b. p. 120°/12 mm., identified by conversion into the corresponding aldehyde, b. p. 128°/15 mm., and oxidation of the latter with silver nitrate to 1-methyl-4-isopropylbenzoic acid, m. p. 69°. The condensation with naphthalene was carried out in presence of light petroleum as a diluent, and a good yield of 1-chloromethylnaphthalene, a colourless liquid having an irritating action on the skin, and boiling at 145—146°/6 mm., was obtained. G. F. M.

**The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. VII. Reactions of 2:5- and 4:5-Dinitro-*m*-xylenes.** KATHLEEN IBBOTSON and JAMES KENNER (*T.*, 1923, 123, 1260—1268).

**The Cryoscopy of Diphenyl in Acetic Acid.** A. BERLANDE (*Bull. Soc. chim.*, 1923, [iv], 33, 466—468).—Experiments on the cryoscopic determination of the molecular weight of diphenyl using glacial acetic acid as solvent are described. The cryoscope employed was not hermetically sealed, and consisted of a stoppered test-tube immersed in an ice-bath, and the stirring was affected by means of the thermometer. The results were too low when the concentration of the solution was such that the freezing-point depression was less than about 0.5°, owing to the progressive hydration of the solvent, which itself caused a lowering of the freezing point of two- to three-hundredths of a degree in ten to

fifteen minutes and only when the depression caused by the diphenyl was sufficiently great to render this negligible, were approximately accurate results obtained. G. F. M.

**Röntgen Ray Spectroscopy of Organic Compounds.** KARL BECKER and HERTA ROSE (*Z. Physik*, 1923, **14**, 369—373).—The following parameters have been determined from crystals of the respective organic substances by X-ray analysis: dibenzyl,  $a:b:c = 2.082:1:1.211$ ,  $\beta = 119^\circ$ ; stilbene,  $a:b:c = 1.077:1:1.415$ ,  $\beta = 118^\circ 40'$ ; benzil,  $a:c = 1:1.652$ ; triphenylmethane,  $a:b:c = 1.140:1:0.578$ ; triphenylcarbinol,  $a:c = 1:0.534$ ; mannitol,  $a:b:c = 1.275:1:0.562$ ; sucrose,  $a:b:c = 1.225:1:0.920$ ,  $\beta = 105.74^\circ$ . The respective numbers of molecules in the unit cell and the corresponding calculated values of the densities are: dibenzyl, 2, 1.185; stilbene, 4, 1.246; benzil, 3, 1.415; triphenylmethane, 3, 1.103; triphenylcarbinol, 6, 1.234; mannitol, 2, 1.555; sucrose, 2, 1.574. In the case of stilbene, the value of  $a$  deduced from X-ray measurements is one half that deduced from goniometric measurements. In the respective cases of triphenylmethane, triphenylcarbinol, and mannitol, the following ratios were found between the respective axial lengths as determined by X-ray and goniometric measurements:  $a$ , 2:1;  $c$ , 3:4;  $a$ , 2:1.

J. S. G. T.

**Dinitronaphthalenes.** V. VESELÝ and K. DVOŘÁK (*Bull. Soc. chim.*, 1923, [iv], **33**, 319—333).—The preparation of the following hitherto inaccessible or unknown dinitronaphthalenes is described: 1:6-Dinitronaphthalene was obtained from 1-nitro-6-aminonaphthalene by replacing the amino-group successively with the diazonium group, and the nitro-group according to the method recently described (A., 1922, i, 690). It melted at  $161-163^\circ$ , and was identical with the compound prepared by Graebe and Drews (A., 1884, 1036). 1:7-Dinitronaphthalene was similarly obtained from 1-nitro-7-aminonaphthalene. It forms small, yellow crystals, m. p.  $156^\circ$ . In like manner 1:4-dinitronaphthalene was obtained from 1-nitro-4-aminonaphthalene. It forms small needles, m. p.  $129^\circ$ . The same reaction applied to 1-nitro- $\beta$ -naphthylamine gave only a diazo-oxide, but 1:2-dinitronaphthalene was obtained from *ar*-1:2-dinitrotetrahydronaphthalene (one of the nitration products of "tetralin") by bromination with 2 mols. of bromine, and heating the dibromo-derivative at  $180^\circ$ , when 2 mols. of hydrogen bromide were eliminated with formation of 1:2-dinitronaphthalene, which forms long, slightly brown needles, m. p.  $158^\circ$ . The hitherto very inaccessible 1:3-dinitronaphthalene was prepared in a similar way from *ar*-1:3-dinitrotetrahydronaphthalene. The partial reduction of 1:6- and 1:7-dinitronaphthalenes with alcoholic stannous chloride resulted in each case in the reduction of the  $\alpha$ -nitro-group, and 6-nitro- $\alpha$ -naphthylamine, red needles m. p.  $167^\circ$ , and 7-nitro- $\alpha$ -naphthylamine, red needles, m. p.  $121-122^\circ$ , were isolated from the respective reaction products. Their acetyl derivatives form yellow crystals melting at  $232-233^\circ$  and  $206-207^\circ$ , respectively. By diazotisation the former naphthyl

mine was converted into 6-nitro- $\alpha$ -naphthol, yellow needles, m. p. 79°. Partial reduction of the above two dinitronaphthalenes with ammonium sulphide, on the other hand, led to the reduction of the  $\beta$ -nitro-group, and formation of 5-nitro- $\beta$ -naphthylamine, and 8-nitro- $\beta$ -naphthylamine, m. p. 104–105°, respectively. The 1:2- and 1:3-dinitronaphthalenes did not behave in a perfectly analogous fashion. Stannous chloride reduced the  $\alpha$ -nitro-group of the 1:3-compound giving 3-nitro- $\alpha$ -naphthylamine, m. p. 136–137°, acetyl derivative, m. p. 255°, but the  $\beta$ -nitro-group of the 1:2-compound is attacked with formation of 1-nitro- $\beta$ -naphthylamine, m. p. 126–127°. Ammonium sulphide reduces 1:3-dinitronaphthalene mainly to the same 3-nitro- $\alpha$ -naphthylamine, together with a small amount of the 4-nitro- $\beta$ -naphthylamine, red needles, m. p. 95°, acetyl derivative, 237–238°. The decomposition of the diazonium salt of 3-nitro- $\alpha$ -naphthylamine gave 3-nitro- $\alpha$ -naphthol, yellow needles, m. p. 167–168°. With 1:2-dinitronaphthalene, ammonium sulphide gave only tarry products. The nitro-group in 1:2-dinitronaphthalene is very mobile, and was replaced by numerous other groups, for example, on boiling with sodium hydroxide 2-nitro- $\alpha$ -naphthol, m. p. 127–128°, was formed. Alcoholic ammonia caused the replacement of the nitro- by the amino-group, with formation of  $\beta$ -nitro- $\alpha$ -naphthylamine, m. p. 41–42°, and on boiling with aniline 2-nitro-1-anilinonaphthalene, orange crystals, m. p. 110–111°, was produced. G. F. M.

**The Crystalline Structure of Anthracene.** (Sir) W. H. RAE (Proc. Physical Soc., 1923, 35, 167–169).—The dimensions of the crystal unit of anthracene have been determined, and the major length of the molecule is found to lie along the  $c$  axis. The differences between the lengths of the  $c$  axis for naphthalene and anthracene is 2.5, which corresponds exactly with the width of the benzene ring. The calculated specific gravity is 1.255, which is in agreement with an experimental determination of this constant. The crystals of naphthalene and anthracene show great similarities; the same planes are in each case the best reflectors, and it is only in the length of the  $c$  axis that there is any great difference. The unit contains two molecules in each case, and since the symmetry number is four, a molecule in the crystal must possess a twofold symmetry. This symmetry has been confirmed by the results.

W. E. G.

**Compounds of Picric Acid with Hydrocarbons.** NIKOLAI EFREMOV (J. Russ. Phys. Chem. Soc., 1918, 50, 373–421).—Binary fusion diagrams are constructed for mixtures of picric acid with various substances. At 50 mol. % formation of the following picrates occurs: Acenaphthere picrate, m. p. 160.8°; acenaphthylene picrate, m. p. 165.3°; phenanthrene picrate, m. p. 132.8°; and  $\beta$ -Chloronaphthalene picrates, m. p. 125.7° and 81.5°, respectively;  $\alpha$ - and  $\beta$ -bromonaphthalene picrates, m. p. 130° and 115°, respectively;  $\alpha$ -benzyl-naphthalene picrate, m. p. 97°, and tene picrate, m. p. 120.9°. Unstable picrates are also formed with

stilbene, transition point, 92.8°, and  $\alpha$ -nitronaphthalene, transition point, 54.7°. Nitroacenaphthene, diphenyl, dibenzyl, diphenylmethane, and triphenylmethane do not form picrates. R. T.

**Compounds of Picryl Chloride with Hydrocarbons.** NIKOLAI N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 421—440).—Binary fusion diagrams are constructed for mixtures of picryl chloride with various hydrocarbons and with picric acid. Equimolecular compounds form in every case with the former, whilst with the latter solid solution, but not compound formation is observed. The following compounds were obtained: Anthracene picryl chloride, m. p. 141.6°; acenaphthene picryl chloride, m. p. 113.2°; acenaphthylene picryl chloride, m. p. 109.4°; retene picryl chloride, m. p. 53.5°; naphthalene picryl chloride, m. p. 91.2°; phenanthrene picryl chloride, m. p. 82.4°, and fluorene picryl chloride, m. p. 64.6°. R. T.

**Compounds of Picramide with Hydrocarbons.** NIKOLAI N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 441—459).—Binary fusion diagrams are constructed for mixtures of picramide with various hydrocarbons and with picric acid. In the latter case, no compound formation occurs, the components forming solid solutions up to 16% of picric acid and 11.5% of picramide. The following equimolecular compounds are formed: Naphthalene picramide, m. p. 168.8°; anthracene picramide, m. p. 158.8°; phenanthrene picramide, m. p. 160.2°; acenaphthene picramide, m. p. 195.4°; retene picramide, m. p. 125.1°; and an unstable equimolecular compound, transition point, 127.5°, exists for fluorene. R. T.

**Some Reactions of Tetranitroaniline.** CECIL WHITEFIELD DAVIES and THOMAS CAMPBELL JAMES (*Aberystwyth Studies*, 1922, 4, 213—216).—Tetranitroaniline does not form compounds with hydrocarbons in dry benzene or acetone solution. With phenol, there is a slight colour change but only with  $\beta$ -naphthol was a definite compound obtained,  $C_6H(NO_2)_4 \cdot NH_2 \cdot C_{10}H_7 \cdot OH$ , deep red needles, beginning to decompose at 110°, m. p. 140°. With primary amines, tetranitroaniline rapidly condenses with elimination of the 3-nitro-group. With aniline, 2:4:6-trinitro-3-aminodiphenylamine is formed, orange-yellow crystals, m. p. 188°. *o*-Toluidine gives 2:4:6-trinitro-3-aminophenyl-*o*-tolylamine, dark red crystals, m. p. 200°; 2:4:6-trinitro-3-aminophenyl-*m*-tolylamine forms brick-red crystals, m. p. 181°, and 2:4:6-trinitro-3-aminophenyl-*p*-tolylamine, orange crystals, m. p. 220°. 2:4:6-Trinitro-3-aminophenyl- $\beta$ -naphthylamine forms bright red crystals, m. p. 212°; from acetone it forms bright yellow crystals containing 1 mol. of acetone which are lost at 70°. When trinitroaniline is warmed with *n*-amyl alcohol, 2:4:6-trinitro-3-aminophenyl amyl ether is obtained, yellow crystals, m. p. 168°. Trinitro-*m*-phenylenediamine is formed when tetranitroaniline is warmed with aqueous ammonia. E. H. R.

**Separation of *o*- and *p*-Nitroacetanilides.** KENKICHI MATSUO and the KÔRÔ SEIYAKU KABUSHIKI KAISHA (Japan. Pat. 3523).—The nitration product of acetanilide is a mixture of about 70% *p*-nitroacetanilide and 30% of the ortho-isomeride. When the mixture is treated with hot water of about 80°, the ortho-isomeride dissolves, whilst the para-isomeride remains insoluble. By filtering, subsequent treatment with hot water if necessary, and washing with hot or cold water, the para-compound, m. p. 208°, is isolated almost quantitatively. The ortho-compound, m. p. 90–93°, is obtained from the mother-liquor and washings by cooling. Formerly it was considered that the para-isomeride is liable to decomposition by treatment with hot water in the presence of acid; the author, however, finds that this compound is stable towards hot water even in the presence of an acid, but the ortho-compound is decomposed to some extent into *o*-nitroaniline by treatment with hot water for a long time in the presence of an acid. K. K.

**The Action of Ferrous Chloride on the Hydrochlorides of some Aromatic Amines.** WILLIAM MURDOCH CUMMING (*J. Soc. Chem. Ind.*, 1923, 42, 166–168t).—The addition of ferrous chloride solution to solutions of the hydrochlorides of certain aromatic amines causes the precipitation of the hydrochlorides, without the formation of double salts. *o*- and *p*-Toluidine hydrochlorides crystallise in a variety of forms according to the conditions of crystallisation, and all these modifications were obtained by using ferrous chloride as precipitant, but after keeping in the mother-liquors for two days the various forms of the ortho-compound were almost completely converted into the rhombic form, and of the para-compound into the rhombohedral form, which modifications appear therefore to be the most stable forms of the hydrochlorides. The phenylenediamine hydrochlorides were not precipitated by ferrous chloride, except when an excess of concentrated hydrochloric acid was present. Ferrous chloride precipitates anhydrous benzidine monohydrochloride from solutions of the dihydrochloride, but from *o*-toluidine dihydrochloride solutions it precipitates a dihydrochloride crystallising with  $1\frac{1}{2}$  mols. of water. Both these salts are much less soluble in water than the normal dihydrochlorides. G. F. M.

**The Effect on the Reaction between Halogenonitrohydrocarbons and Aniline of Different Substituents in the Latter.** B. LINKE (*Ber.*, 1923, 56, [B], 848–851).—The velocity of reaction between chloronitrohydrocarbons and substituted anilines, occurring in accordance with the general scheme,  $2\text{PhNH}_2 + \text{C}_6\text{H}_4\text{ClNO}_2 = \text{NH}_2\text{Ph.HCl} + \text{NO}_2\text{C}_6\text{H}_3\text{NHPh}$ , has been investigated in alcoholic solution by determining the hydrochloric acid liberated after definite intervals of time as silver chloride. 4-Chloro-1-nitrobenzene, 4-chloro-1:3-dinitrobenzene, and 2-chloro-1:3:5-trinitrobenzene have been used on the one hand, and *o*-, *m*-, and *p*-nitro-, chloro-, bromo-, and iodo-anilines, the aminophenols, toluidines, phenylenediamines, aminobenzoic acids, aminobenzenesulphonic acids in addition to *p*-phenetidine, on the other.

The reactivity of the amines is diminished by the presence in them of iodine, bromine, chlorine, nitro-, sulphonic, or carboxylic groups, the effect of the two latter being less pronounced than that of the other four. The action of the substituent is least marked when it is in the meta-position to the amino-group, and most marked in the ortho-position. With regard to the other substituents investigated (OH, Me, and  $\text{NH}_2$ ), the most pronouncedly restrictive action is observed, as in the previous cases, when they are in the ortho-position, but the least action when they are in the para-position. The action of the amino-group is less marked than that of any other substituent.

The following compounds have been incidentally prepared: 2-Iodo-2':4'-dinitrodiphenylamine, golden-yellow, fibrous aggregates, m. p. 164—165°; 3-Iodo-2':4'-dinitrodiphenylamine, orange-coloured, rhombic crystals, m. p. 135°; 4-Iodo-2':4'-dinitrodiphenylamine, orange-coloured crystals, m. p. 185°; 2-Iodo-2':4':6'-trinitrodiphenylamine, orange-coloured, rhombic needles, m. p. 206°; 3-Iodo-2':4':6'-trinitrodiphenylamine, golden-yellow platelets, m. p. 150—152°; 4-Iodo-2':4':6'-trinitrodiphenylamine, golden-yellow, fibrous aggregates, m. p. 196°; 2-Chloro-2':4':6'-trinitrodiphenylamine, orange-coloured, rhombic crystals, m. p. 160—161°; 2-Bromo-2':4':6'-trinitrodiphenylamine, small, orange-coloured, rhombic leaflets or needles, m. p. 187—189°; 2-Methyl-2':4'-dinitrodiphenylamine, red, microcrystalline needles, m. p. 158—159°; 3-Methyl-2':4':6'-trinitrodiphenylamine, carmine-red aggregates, m. p. 119°.

H. W.

**The Mutual Replacement of Ammonia and Aniline in Amino-derivatives of Triphenylmethane.** PAVEL IVANOVITCH PETRENKO-KRITSCHENKO and A. GANDELMAN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 413—417).—Triphenylmethylaniline,  $\text{NHP}(\text{C}_6\text{H}_5)_3$ , is converted by heating in a sealed tube with alcoholic ammonia into triphenylmethylaniline, which can be reconverted into the former substance by heating with excess of aniline. Triphenylmethylcarbinol cannot be an intermediate product in these reactions, as on similar treatment with ammonia or aniline these substances are not produced. Triphenylmethylaniline can be more easily converted into triphenylmethylaniline by boiling with a solution in acetic acid of ammonium acetate. The reverse reaction does not, however, appear to take place. Triphenylmethylcarbinol, when treated in this way with ammonium or aniline acetate, gives fair yields of the corresponding amines.

R. T.


**Oxidations and Reductions Caused by Salts of Uranium under the Influence of Light. Antioxygen Action of Phenols.** JULES ALOY and VALDIGUÉ (*Compt. rend.*, 1923, 176, 1229—1231).—Oxidations and reductions brought about by uranium compounds under the influence of light are closely related to the changes which the uranium salt itself undergoes. Thus when alcohol or dextrose is added to a 1% solution of uranium acetate, the former is oxidised and the latter reduced to the violet oxide,  $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ . If, in addition, methylene-blue is added to the above solution, the

dextrose is oxidised and the methylene-blue reduced, the uranium salt playing the rôle of an oxido-reducing catalyst. Aldehydes and the lower fatty alcohols can all be similarly oxidised, and the progress of the reaction can be followed by the reduction of the uranium acetate or of methylene-blue. The phenols, although readily oxidisable in ordinary circumstances, behave anomalously, owing to the antioxygen character of these substances, and they are neither oxidised themselves nor do they permit the oxidation of other substances to proceed. A red coloration is produced on adding the uranium compound to the phenol solution, but no other apparent change occurs. The solution does, however, contain a certain amount of uranous salt and the violet oxide can be precipitated from it by heating at  $100^{\circ}$ . G. F. M.

**Binary Systems of  $\alpha$ - and  $\beta$ -Forms of Chloroacetic Acid with Phenols.** IV. EFISIO MAMELI and GLAUCO COCCONI (*Gazzetta*, 1923, 53, i, 149—158; cf. A., 1913, ii, 571).—With the various phenols examined, neither the  $\alpha$ - nor  $\beta$ -form of chloroacetic acid forms additive compounds, the two acids behaving as acids of medium strength.

The fusion curve, and the position of the eutectic, for the systems phenol- $\beta$ -chloroacetic acid and *o*-cresol- $\beta$ -chloroacetic acid agree with those given by Kendall (A., 1916, i, 599) for the corresponding systems containing the  $\alpha$ -form of the acid. Data are given also for the binary systems formed by each of these acids with *m*- and *p*-cresols,  $\alpha$ - and  $\beta$ -naphthols, thymol, and guaiacol. T. H. P.

**Action of Organo-magnesium Compounds on Amino-phenols.** E. PUXEDDU (*Gazzetta*, 1923, 53, i, 99—105).—The action of magnesium ethyl bromide on 3-amino-*p*-cresol or amino- $\beta$ -naphthol differs from that on a compound containing an amino- or a phenolic group alone. In either case, gas is generated, two molecules of the Grignard reagent reacting with one molecule of the aminophenol, probably with formation of an additive compound,  $\text{OH}, \text{MgEtBr}$

pound of the type   $\text{NH}_2, \text{MgEtBr}$ . When treated with acetyl chloride, these products yield the corresponding diacetyl derivatives.

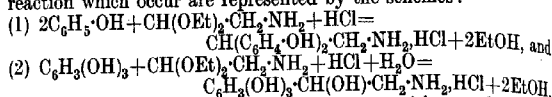
The acetyl derivative of 3-acetyl-amino-*p*-cresol,  $\text{OAc} \cdot \text{C}_6\text{H}_3\text{Mc} \cdot \text{NHAc}$ , forms crystals, m. p.  $157^{\circ}$ . T. H. P.

**Imino-aryl Ethers. II. The Thermal Decomposition of *N*-Arylaryliminoaryl Ether Hydrochlorides.** ARTHUR WILLIAM CHAPMAN (T., 1923, 123, 1150—1155).

**Nitro-derivatives of *m*-Cresol.** GEORGE PHILIP GIBSON (T., 1923, 123, 1269—1277).

**The Reaction of Aminoacetals with Phenols and Phenolic Ethers.** O. HINSBERG (*Ber.*, 1923, 56, [B], 852—857).—The introduction of the groups  $-\text{CH}_2\text{CH}_2\text{NH}_2$  or  $-\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$  into the aromatic nucleus is of considerable importance in pharmacological chemistry. It can be effected by allowing aminoacetal or its *N*-alkylated substitution products to react with phenols

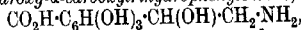
or phenolic ethers in the presence of hydrochloric or acetic and sulphuric acids as condensing agents. The two main types of reaction which occur are represented by the schemes:



The former reaction generally predominates with monohydroxy-, the latter with polyhydroxy-phenols, but its course can be altered in either case by suitable adjustment of the experimental conditions.

$\beta$ -Amino- $\alpha$ -di-4-hydroxyphenylethane,  $CH(C_6H_4\cdot OH)_2\cdot CH_2\cdot NH_2$ , is prepared by the action of concentrated hydrochloric acid at  $100^\circ$  on a mixture of aminoacetal and phenol. It crystallises in colourless needles, which are stable towards air, m. p.  $105^\circ$ ; the hydrochloride, a colourless, hygroscopic mass, and the chloroplatinate, brownish-yellow needles, are described.  $\beta$ -Amino- $\alpha$ -di-4-hydroxy-2-methyl-3-isopropylphenylethane, from aminoacetal and thymol, forms colourless needles, m. p.  $220^\circ$ ; it yields a hydrochloride (+ $2H_2O$ ), colourless needles.  $\beta$ -Amino- $\alpha$ -di-2-hydroxy-1-naphthylethane, colourless needles, m. p.  $124^\circ$ , and its hydrochloride, colourless needles, are described.

Methylaminoacetal reacts with two molecular proportions of pyrocatechol in the presence of concentrated hydrochloric acid at the atmospheric temperature to give  $\beta$ -methylamino- $\alpha$ -di-o-dihydroxyphenylethane,  $(C_6H_3(OH)_2)_2CH\cdot CH_2\cdot NHMe$ , colourless needles, m. p.  $143^\circ$ , which yields a hydrochloride, colourless needles, sparingly soluble in hydrochloric acid. If, however, molecular proportions of methylaminoacetal and pyrocatechol are heated with hydrochloric acid and water in a sealed tube at  $100^\circ$ , r- $\beta$ -methylamino- $\alpha$ -hydroxy- $\alpha$ -o-dihydroxyphenylethane,  $(HO)_2C_6H_3\cdot CH(OH)\cdot CH_2\cdot NHMe$ , is obtained; the free base is unstable when exposed to air, but yields a stable hydrochloride which is freely soluble in water. r- $\beta$ -Amino- $\alpha$ -hydroxy- $\alpha$ -o-dihydroxyphenylethane is obtained as the hydrochloride from pyrocatechol and aminoacetal. Pyrogallol and aminoacetal yield the unstable r- $\beta$ -amino- $\alpha$ -hydroxy- $\alpha$ -trihydroxyphenylethane (the hydrochloride crystallises in colourless needles). r- $\beta$ -Amino- $\alpha$ -hydroxy- $\alpha$ -carboxytrihydroxyphenylethane,



is isolated as the hydrochloride from the product of the action of gallic acid on aminoacetal.

$\beta$ -Amino- $\alpha$ -diphenylethane, which could not be obtained in the crystalline condition, is the main product of the action of aminoacetal on phenetole in the presence of sulphuric and acetic acids.  $\beta$ -Methylamino- $\alpha$ -bis-o-dimethoxyphenylethane is non-crystalline; it gives a hydrochloride, small, colourless needles, m. p.  $102^\circ$ .  $\beta$ -Amino- $\alpha$ -hydroxy- $\alpha$ -trimethoxyphenylethane, from aminoacetal and pyrogallol trimethyl ether, gives a hydrochloride, colourless crystals, m. p.  $187^\circ$ , and a chloroplatinate, pale yellow plates.  $\beta$ -Amino- $\alpha$ -bistrimethoxyphenylethane hydrochloride forms large, colourless crystals, m. p.  $199^\circ$ ; the free base has little tendency towards crystallisation.

H. W.

**Catalytic Ammonolysis of  $\beta$ -Naphthol and Chlorobenzene in the State of Vapour.** A. M. HOWARD and ALEXANDER LOWY (*J. Ind. Eng. Chem.*, 1923, 15, 397—401).— $\beta$ -Naphthol and chlorobenzene vapours mixed with ammonia were passed at definite temperatures over various contact materials. For  $\beta$ -naphthol, alumina was the best catalyst, and yields of 90—95% of  $\beta$ -naphthylamine were obtained under suitable conditions. The activity of the catalyst increased very rapidly from 400° to an optimum temperature range of 430—450°, and the best yields of the primary amine were obtained when the  $\beta$ -naphthol was heated at 191—193° in the vapour of boiling dimethylaniline, and a slow stream of ammonia gas was bubbled through. If the rate of flow of the vapour mixture was too great, equilibrium was not attained during its passage over the catalyst, and lower yields resulted. Using pure ammonia, the catalyst did not depreciate materially in activity during a run of sixteen hours' duration. About 5% of  $\beta\beta$ -dinaphthylamine was obtained as a by-product. Experiments were conducted with titania and thoria as catalysts, but the results were inferior to the above. In the experiments with chlorobenzene, some conversion to aniline was effected with reduced nickel or iron catalysts at 380° and 450°, respectively, but the catalysts were soon poisoned, and the original yields of about 7% rapidly fell off to mere traces. Reduced cobalt, copper, and platinum black gave still less satisfactory results. G. F. M.

**Boric Acid Compounds of some Organic Substances containing more than One Hydroxyl Group. Boron as a Quinquevalent Element.** P. H. HERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 32—42).—By the action of boric acid on  $\beta\beta$ -dimethylpentane- $\beta\delta$ -diol, a compound is obtained which crystallises with great facility, m. p. 100—102°, and must have the formula  $\text{CH}_2 \begin{smallmatrix} \text{CMe}_2\text{O} \\ \text{CMe}_2\text{O} \end{smallmatrix} \text{B}\cdot\text{OH}$ . It has a saffron-like odour, and is

a weak acid no stronger than boric acid. It was supposed from the latter observation that the strong acids which are formed by addition of many polyhydroxy-compounds to boric acid solutions must have a different constitution from the above compound. In confirmation of this view, weakly acidic boric acid compounds similar to the above were obtained from  $\beta\delta$ -dimethylhexane- $\beta\delta$ -diol and pinacone. Evidence of the formation of compounds with trimethylene glycol, ordinary glycol, and *cis*-cyclohexane-1:2-diol was also obtained, but the compounds could not be crystallised. All these compounds appear to be partly split up into their components in aqueous solution. In the case of the *cis*-cyclohexane-1:2-diol boric acid compound, a crystalline potassium salt was obtained. This has an alkaline reaction and the potassium can be titrated quantitatively in presence of methyl-orange. A dipotassium derivative of this compound was also obtained. Crystalline potassium salts of the boric acid compounds of *cis*-hydrindene-1:2-diol, *cis*-cyclopentane-1:2-diol, *cis*-tetrahydronaphthalene-1:2-diol, and -2:3-diols were also obtained, but they could not always be obtained free from potassium hydroxide on account of their high

solubility in water and in alcohol. These compounds provide a method for separating *cis*- from *trans*-cyclic-1 : 2-diols, as the latter do not give such compounds.

The crystalline potassium salt of pyrocatecholboric acid prepared by Böeseken, Haefen, and Obreen (A., 1918, i, 219) has been analysed again, as its composition was uncertain. It is now found to be  $C_{12}H_8O_4BK$  and the only plausible structure is  $\left[ C_6H_4 \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} \right]_2 BK$ .

The boron is here quinquivalent or, from another point of view, has the co-ordination number four. Although this salt has an alkaline reaction, the potassium cannot be titrated quantitatively; pyrocatecholboric acid is therefore a stronger acid than the other diol compounds described above. It is probable that other complex acids stronger than boric acid have a structure similar to that proposed for pyrocatecholboric acid. Free *pyrocatecholboric acid* can be obtained by heating the aniline salt in a vacuum, and can be purified by sublimation in a vacuum at 200°.

The boric acid compound of *cis*-cycloheptane-1 : 2-diol (cf. Derr, A., 1922, i, 651) forms an oil with a saturated solution of boric acid. On addition of aniline to the oil, it crystallises, forming an unstable aniline salt,  $C_{20}H_{38}O_4NB$ . This appears to be *aniline di-cis-cycloheptane-1 : 2-diolborate*. Scheibe's potassium borodicitrate and Jahn's zinc borodisalicylate are also probably derivatives of quinquivalent boron. The structure of these compounds is further discussed by Böeseken (this vol., ii, 406). E. H. R.

#### Ethylene and Trimethylene Ethers of Dihydroxybenzenes.

I. MORITZ KOHN and FRANZ WILHELM (*Monatsh.*, 1923, 43, 545—555).—Molecular amounts of ethylene bromide and aqueous potassium hydroxide when refluxed with a large excess of resorcinol yield *di-resorcinol ethylene ether*,  $C_6H_4(O-C_2H_4-OH)_2$ , in fair yield as colourless, thin needles, m. p. 163°; the *benzoyl* derivative has m. p. 115—116°. With methyl sulphate and potassium hydroxide the *dimethyl ether*,  $C_6H_4(O-C_2H_4-OMe)_2$ , m. p. 61—63°, is formed, which is identical with the product obtained from resorcinol monomethyl ether and ethylene bromide in presence of sodium ethoxide. In a similar manner, trimethylene bromide refluxed with aqueous potassium hydroxide and resorcinol in large excess yields *di-resorcinol trimethylene ether*,  $C_6H_4(O-C_3H_4-OH)_2$ , long needles, m. p. 118°; *benzoyl* derivative, m. p. 97—98°. With methyl sulphate and potassium hydroxide it yields the dimethyl ether,  $C_6H_4(O-C_3H_4-OMe)_2$ , m. p. 39—41°, identical with the product from resorcinol monomethyl ether and trimethylene bromide in presence of sodium ethoxide. Ethylene bromide and aqueous potassium hydroxide refluxed with a large excess of pyrocatechol yield, however, only the cyclic ethylene ether,  $C_6H_4O_2C_2H_4$ , previously obtained by Vorländer (A., 1895, i, 17), and not the unknown bisdipyrocatechol trimethylene ether. Using trimethylene bromide, however, *dipyrocatechol trimethylene ether* is readily obtained in rhombic needles [ $\alpha$ :  $\beta$ :  $\gamma$ :  $\delta$  = 0.5047 : 1 : 0.6178], m. p. 123—125°, benzoyl derivative, m. p. 91—93°. On methylation, it yields a dimethyl ether identical with Gattermann's diguaiacol-trimethylene ether, obtained from

guaiacol and trimethylene bromide in presence of sodium ethoxide, m. p. 107—109° (111—112° ?) (A., 1908, i, 35). Quinol in large excess when refluxed with aqueous alkali hydrate and ethylene dibromide or trimethylene dibromide yields, respectively, Vorländer's diquinol ethylene ether and the new substance, *diquinol trimethylene ether*, m. p., respectively, 222—24° (Vorländer 219—220°), and 142—144°. The *ethylene* derivative forms a *dimethyl ether*, m. p. 148—150°, and a *benzoyl* derivative, m. p. 186°; the *trimethylene* derivative forms a *dimethyl ether*, m. p. 84—85°, and a *benzoyl* derivative, m. p. 138—139°. The methyl ethers are identical with the products obtained from quinol monomethyl ether and ethylene dibromide or trimethylene bromide, respectively, in presence of sodium ethoxide. F. A. M.

**Ethylene and Trimethylene Ethers of the Dihydroxybenzenes.** II. MORITZ KOHN and LEOPOLD SAFRIN (*Monatsh.*, 923, 49, 557—568; cf. preceding abstract).—*Phenyl o-hydroxyphenyl ethylene ether*,  $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , is obtained on refluxing  $\beta$ -bromophenetole with a large excess of pyrocatechol and a little water, and adding the calculated amount of aqueous potassium hydroxide during half an hour; it forms crystals, m. p. 86.5°. Methylation by means of methyl sulphate yields the corresponding *phenyl o-anisyl ethylene ether*,  $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , long needles, m. p. 86—87°, which is identical with the product formed from guaiacol and  $\beta$ -bromophenetole in presence of sodium ethoxide. The *benzoyl* derivative,  $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ , forms colourless prisms, m. p. 60—61°.

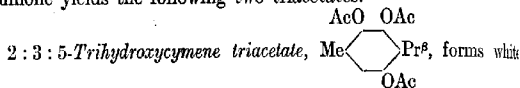
On treatment of the original phenyl *o*-hydroxyphenyl ethylene ether with a further molecule of  $\beta$ -bromophenetole in presence of sodium ethoxide, the substance *pyrocatechol bisphenoxyethyl ether* is formed,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OPh})_2$ , forming platelets, m. p. 116—117°. The action of ethylene bromide on phenyl *o*-hydroxyphenyl ethylene ether in presence of sodium ethoxide yields the *bis- $\beta$ -phenoxy- $\gamma$ -ethoxyphenyl ethylene ether*,  $[\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}]_2\text{C}_2\text{H}_4$ , short, thin needles, m. p. 106—107°; if trimethylene bromide is used in place of ethylene bromide, the product is the *trimethylene bis- $\beta$ -phenoxy- $\gamma$ -ethoxyphenyl ether*,  $[\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}]_2\text{C}_3\text{H}_6$ , needles, m. p. 11°; the latter substance is also formed by the action of  $\beta$ -bromophenetole on dipyrocatechol trimethylene ether in presence of sodium ethoxide.

By refluxing phenyl  $\gamma$ -bromopropyl ether with a large excess of pyrocatechol in presence of a little water and the calculated quantity of potassium hydroxide, there is formed *phenyl o-hydroxyphenyl trimethylene ether*,  $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , thick prisms, m. p. 56—57°; the *methoxy-ether* has m. p. 55—56°; the *benzoyl* derivative, needles, m. p. 60—61°. It reacts with a second molecule of phenyl  $\gamma$ -bromopropyl ether in presence of sodium ethoxide to form *pyrocatechol bisphenoxypropyl ether*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OPh})_2$ , needles, m. p. 51°; or using  $\beta$ -bromophenetole in place of phenyl  $\gamma$ -bromopropyl ether, the product is *pyrocatechol  $\beta$ -phenoxyethyl phenoxypropyl ether*,  $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_3\text{H}_6\cdot\text{OPh}$ , prisms, m. p. 63—67.5°; the latter substance is also obtained by the converse

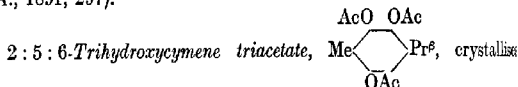
method from phenyl *o*-hydroxyphenyl ethylene ether and phenyl  $\gamma$ -bromopropyl ether. Two molecules of phenyl *o*-hydroxyphenyl trimethylene ether may be united by means of ethylene dibromide or trimethylene dibromide in presence of sodium ethoxide to yield, respectively, the substances *bis*- $\gamma$ -phenoxy-*o*-propoxyphenyl ethylene ether,  $C_6H_4(O-C_6H_4-O-C_3H_6-O-Ph)_2$ , needles, m. p. 102–103°, and *bis*- $\gamma$ -phenoxy-*o*-propoxyphenyl trimethylene ether,  $C_6H_4(O-C_6H_4-O-C_3H_6-O-Ph)_2$ , needles, m. p. 61–62°. The latter product is also formed from two molecules of phenyl  $\gamma$ -bromopropyl ether and one molecule of pyrocatechol trimethylene ether in presence of sodium ethoxide.

F. A. M.

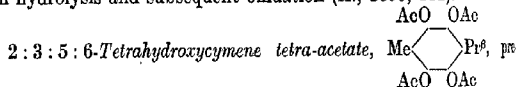
**Investigations on Phenols Derived from Cymene.** G. BARGELLINI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 231–235).—Thiele (A., 1898, i, 469) has shown that a new hydroxyl group may be introduced into the molecule of a quinol by treating the corresponding quinone with acetic anhydride in presence of a small amount of sulphuric acid. Application of this reaction to thymoquinone yields the following two triacetates.



crystals, m. p. 135–137°, and, on hydrolysis and subsequent oxidation, gives the 3-hydroxythymoquinone described by Mazzar (A., 1891, 297).



in white needles, m. p. 83–85°, and yields 6-hydroxythymoquinone on hydrolysis and subsequent oxidation (A., 1890, 884).



pared by the action of acetic anhydride in presence of a little sulphuric acid on either 3- or 6-hydroxythymoquinone or, better by oxidising either of these compounds to dihydroxythymoquinone m. p. 222–224°, and heating the latter with acetic anhydride and zinc dust, crystallises in white leaflets, m. p. 186–188°.

When dihydroxythymoquinone is reduced in alcoholic solution by means of hydrogen in presence of platinum black, the red solution absorbs hydrogen and is completely decolorised, but in contact with the air it rapidly reddens, the tetrahydroxycymene probably formed undergoing oxidation to the original dihydroxythymoquinone (cf. Henderson and Boyd, T., 1910, 97, 1663).

T. H. P.

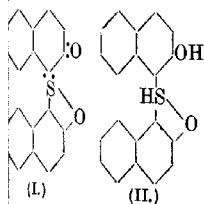
**Photo-sensitiveness of certain Urethanes.** A. KORCZYNSKI (*Gazzetta*, 1923, 53, i, 94–99).—Urethanes have been prepared by the action of diphenylcarbamide chloride on the following phenols: *p*-chloro-, bromo-, and iodo-phenols, *o*- and *p*-nitrophenols, 4-chloro-

and 4-bromo-2-nitrophenols, 4:6-dibromo- and 4:6-di-iodo-2-nitrophenols, 4-chloro-6-bromo-2-nitrophenol, 2:6-dichloro-4-nitrophenol, and 2:4:6-trichlorophenol. Photo-sensitiveness is shown by the compounds obtained from the halogenated nitrophenols with an ortho-nitro-group and a para-halogen atom, but not by those obtained from the halogenated or nitro-phenols; in the former case, introduction of a second halogen atom in the second ortho-position leaves the photo-sensitiveness unchanged. The photochemical change occurring in these compounds is more destructive than the similar phenomenon observed, for instance, with *o*-nitrobenzaldehyde (Ciamician and Silber, A., 1901, i, 390, 547; 1902, i, 434), since the nitroso-compound cannot be isolated; no marked change occurs, however, in the diphenylaminic portion of the molecule. The fact that the condensation of 2:4-dinitrophenol or of picric acid with diphenylcarbamide chloride yields, not the corresponding carbamic ester, but a non-homogeneous, resinous mass, is explainable by the occurrence of a photochemical reaction.

[With Sr. GRZYBOWSKI.]—4-Chlorophenyl N-diphenylcarbamate,  $C_6H_4ClO-CO-NPh_2$ , forms colourless needles, m. p.  $97^\circ$ ; the 4-bromophenyl ester, colourless needles, m. p.  $99^\circ$ ; the 4-iodophenyl ester, m. p.  $126-127^\circ$ ; the 2:4:6-trichlorophenyl ester, colourless needles, m. p.  $143^\circ$ ; the 2-nitrophenyl ester, colourless crystals, m. p.  $108-109^\circ$ ; the 4-nitrophenyl ester, colourless needles, m. p.  $112^\circ$ ; the 2:6-dichloro-4-nitrophenyl ester, colourless needles, m. p.  $132^\circ$ ; the 4-chloro-2-nitrophenyl ester, m. p.  $124-125^\circ$ , is photo-sensitive; the 4-chloro-6-bromo-2-nitrophenyl ester, m. p.  $140^\circ$ , is photo-sensitive; the 4:6-dibromo-2-nitrophenyl ester, m. p.  $139^\circ$ , is photo-sensitive; the 4:6-di-iodo-2-nitrophenyl ester, m. p.  $174-175^\circ$ ; the 4-bromo-2-nitrophenyl ester forms lustrous, colourless needles, m. p.  $129-130^\circ$ , and is photo-sensitive, both in the crystalline condition and in solution in neutral solvents such as benzene, toluene, ethyl or amyl alcohol, and also in absence of oxygen. T. H. P.

#### The Isomerism of $\beta$ -Naphthol Sulphide and the Analogous Isomerism of Aromatic *o*-Hydroxysulphides.

RUDOLF LESSER and GEORG GAD (*Ber.*, 1923, 56, [B], 963-978).—The isomerism of  $\beta$ -naphthol sulphides has been examined in detail by Smiles and his co-workers (T., 1911, 99, 973; 1912, 101, 710; 1146, 1420; 1913, 103, 340, 901; 1914, 105, 1396, 1739, 1744), and by Hinsberg (A., 1915, i, 237, 808; 1916, i, 723). The former has drawn the conclusion that it is due to the mode of union within



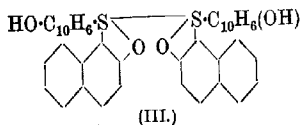
the naphthalene nuclei, the latter that it is caused by the structure of the sulphur atom itself. It is now shown, however, that the isomerism is not of an abnormal type, since if the constitution (I) assigned by Hinsberg to the dehydrosulphide is adopted it is readily possible that this may pass on reduction into the compound II without rupture of the "thionylum" (the term is applied by the authors to the structure,

$-\text{CH} \begin{smallmatrix} > \text{S} < \\ \text{CH} & \text{O} \end{smallmatrix}$ ). This constitution is in complete harmony with the behaviour of the isosulphide. The ability to form dehydro-compounds, and hence also isosulphides, is not restricted to naphthalene derivatives, but is common to aromatic *o*-hydroxy-sulphides which have a substituent in the para-position to the hydroxy-group and a tertiary carbon atom in the ortho-position to the sulphur atom.

During the course of the work it has been frequently necessary to chlorinate phenols in order to introduce a substituent into the para-position. This has been effected by sulphuryl chloride, but it has been observed that reaction does not occur, at any rate under the usual conditions, if the phenol contains a negative substituent in the ortho-position to the hydroxy-group as in *o*-chlorophenol, *o*-nitrophenol, salol, *o*-hydroxydiphenyl, *o*-chloro-*s-m*-xylene. The general assumption that sulphuryl chloride only chlorinates phenols in the para-position is shown to be incorrect, since ortho-derivatives are simultaneously produced in varying amounts. The chlorides of sulphur do not react with phenols which contain a negative substituent in the ortho-position to the hydroxy-group and a substituent in the para-position such as dichloro-*s-m*-xylene, *p*-chloro-*o*-nitrophenol, *o*-chloro-*p*-nitrophenol and *o*-nitro-*p*-cresol.

With regard to the nomenclature of the group, the authors propose to retain the terms "dehydrosulphide" and "isosulphide," and to distinguish between the dehydro-compounds which contain a single and double thionylum ring by appending in brackets the expressions "quinoid form" (as in formula I) and "spiran form" (as in formula IV).

$\beta$ -Naphthol sulphide, its dihydro-compound, and the isosulphide are prepared in the usual manner. The latter is oxidised by iodine



to diiso- $\beta$ -naphthol sulphide (annexed formula III), m. p. 141–142°, which is identical with the compound obtained by Hinsberg by the action of hydrogen peroxide on the isosulphide. It is converted by benzoyl chloride and sodium hydroxide into the corresponding dibenzoate, yellow platelets (+C<sub>6</sub>H<sub>5</sub>), m. p. 202–203°, which is reduced by zinc dust and hydrochloric acid to *o-monobenzoyliso- $\beta$ -naphthol sulphide*, pale yellow prisms, m. p. 111–112°, which is reconverted by iodine into the parent dibenzoate. The isomeric *S-monobenzoyliso- $\beta$ -naphthol sulphide*, pale yellow platelets m. p. 181°, is prepared from the isosulphide and benzoyl chloride in the presence of pyridine, and is converted into *dibenzoyliso- $\beta$ -naphthol sulphide*, colourless platelets, m. p. 179–180°, which is also obtained from the *O*-benzoyl compound or from the isosulphide itself. *Monobenzoyl- $\beta$ -naphthol sulphide* crystallises in colourless lustrous platelets, m. p. 190°, whereas the corresponding *p-benzoyl* derivative forms small, colourless needles, m. p. 195°.

**6-Bromo-2-naphthol sulphide**, long, colourless needles, m. p. 245—46°, is prepared by the action of sulphur chloride on 6-bromo-naphthol suspended in carbon disulphide. The corresponding *dibenzoyl* compound crystallises in colourless, felted needles, m. p. 70°. The sulphide is oxidised by potassium ferricyanide in alkaline solution to *dehydro-6-bromo-2-naphthol sulphide* (*quinoid form*), ruby-red, cubic crystals, m. p. 176—177° [*mono-p-nitro-phenylhydrazone*, orange-yellow needles, m. p. 254° (decomp.)], which is reduced by zinc dust in the presence of benzene and hydrochloric acid to *iso-6-bromo-2-naphthol sulphide*, pale yellow platelets, m. p. 156—157° (*dibenzoyl* derivative, small, colourless needles, m. p. 184—185°).

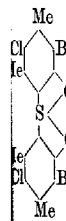
**Methyl 2-hydroxynaphthalene-3-carboxylate 1-sulphide** forms lemon-yellow crystals, m. p. 227—228° (*dibenzoate*, colourless platelets, m. p. 231—232°); it is oxidised by bromine to the *dehydro*-compound (*spiran form*) (annexed formula IV), dark red crystals, m. p. 245—246°, which is reduced by zinc dust and hydrochloric acid in the presence of benzene to *methyl iso-2-hydroxynaphthalene-3-carboxylate-1-sulphide*, yellow crystals, m. p. 227—228°, which appears to pass below its melting point into the normal sulphide; the corresponding *dibenzoyl* derivative forms yellow crystals, m. p. 176°.

(IV.)

*s-m*-Xylenol, dissolved in chloroform, is converted by the theoretically necessary amount of sulphuryl chloride into a mixture of 2-chloro-*s-m*-xylenol, long, colourless prisms, m. p. 115—116°, and minor quantities of 6-chloro-*s-m*-xylenol, colourless needles, m. p. 49—50°; an excess of the reagent produces *dichloro-s-m*-xylenol, m. p. 95—96°. The *p*-chloro-derivative is converted by sulphur chloride in the presence of chloroform into 2-chloro-*s-m*-xylenol 4-sulphide, small, colourless needles, m. p. 214—215°, which

is transformed successively by bromine in the presence of alkali hydroxide into 2-chloro-6-bromoxylene 4-sulphide, colourless, lustrous needles, m. p. 215—216°, and *dehydro-2-chloro-6-bromo-s-m-xylene sulphide* (*spiran form*) (annexed formula), coarse, dark red crystals, m. p. 195° (the mother-liquors from the crystals contain 2-chloro-4:6-dibromo-*s-m*-xylenol, long, asbestos-like needles, m. p. 158°). The *dehydro*-compound is converted by zinc dust and hydrochloric acid in the presence of benzene into *iso-2-chloro-6-bromo-s-m-xylene 4-sulphide*, pale yellow prisms, m. p. 177°, which is oxidised smoothly by iodine in the presence of sodium hydrogen carbonate solution to *diiso-2-chloro-6-bromo-s-m-xylene sulphide*, pale yellow, cubic crystals, m. p. 127° (decomp.).

*p*-Xylenol is converted by sulphuryl chloride in the presence of chloroform into *chloro-p-xylene*, needles, m. p. 74—75°, after previous softening, which is transformed by sulphur chloride into *chloro-p-xylene sulphide*, colourless needles, m. p. 180—181°. *Chlorothymol sulphide*, [S : OH : C<sub>3</sub>H<sub>7</sub> : Cl : Me = 2 : 3 : 4 : 6 : 1], forms



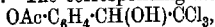
large, glassy crystals, m. p. 110—111°. *φ-Cumenol sulphide* crystallises in colourless, lustrous needles, m. p. 127—128°. The sulphides described in this paragraph are oxidisable to coloured dehydro-compounds.

The following phenolic sulphides do not contain a substituent in the ortho-position to the sulphur atom and do not yield dehydro-compounds: *m-Xylenol sulphide*, almost colourless prisms, m. p. 96—98°; *6-chloro-m-cresol sulphide*, colourless, lustrous needles, m. p. 180—181°.

H. W.

**Aldol Condensation between Chloral and Phenols.** H. PAULY and HEINRICH SCHANZ (*Ber.*, 1923, 56, [B], 979—985).—Aldol condensations between aldehydes and phenols have only been observed previously between exceptionally reactive members of these classes of compounds. The type of change, however, appears to be general, since chloral is found to react in this manner with a number of phenols. The phenolic hydroxy-group remains intact in the new compounds.

Chloral hydrate and phenol are melted together, and so much powdered potassium carbonate is added to the mixture that litmus paper is just turned blue, after which it is preserved for six weeks at the atmospheric temperature, during which time *4-hydroxy-phenyltrichloromethylcarbinol*,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ , needles, m. p. 87°, slowly separates. The corresponding *monoacetate*,



crystallises in needles, m. p. 173°. The constitution of the condensation product is deduced from the observation that it is converted by phenol in the presence of glacial acetic and concentrated sulphuric acids into the previously described  $\beta\beta$ -trichloro- $\alpha\alpha$ -bis-*p*-hydroxyphenylethane, m. p. 202°. Under similar conditions, *p*-cresol gives *p-tolyltrichloromethylcarbinol*, colourless needles, m. p. 147—148°, and guaiacol yields *4-hydroxy-3-methoxyphenyltrichloromethylcarbinol*, colourless needles, m. p. 118—119° (*monoacetate*, slender needles, m. p. 124°). The constitution assigned to the latter substance is deduced from its conversion into vanillin. *Trichlorodiguaiacylthane* is prepared from the guaiacolcarbinol and guaiacol or from chloral and guaiacol in the presence of glacial acetic and concentrated sulphuric acids; it is non-crystalline and does not exhibit a definite melting point. It separates from carbon tetrachloride in colourless needles ( $+\text{CCl}_4$ ), m. p. 98°, and from chloroform ( $+\text{CHCl}_3$ ) in slender needles. It is converted by reduction with zinc dust into *4:4'-dihydroxy-3:3'-dimethoxystilbene* (?), slender needles, m. p. 200°. Pyrocatechol and chloral yield *2:3-(or 3:4)-dihydroxyphenyltrichloromethylcarbinol*, small, colourless needles, m. p. 128—129°, whereas resorcinol and chloral hydrate give *2:4-dihydroxyphenyltrichloromethylcarbinol*, colourless needles, m. p. 176°.

H. W.

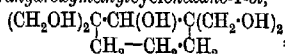
**The Action of Magnesium on a Mixture of Bromoallene with Cuminol.** K. VOLKOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 259—263).—*Cumylallylcarbinol*,  $\text{C}_6\text{H}_4\text{Pr}^s\cdot\text{CH}(\text{C}_3\text{H}_5)\cdot\text{OH}$ , b. p.

140°/17.5 mm.,  $d_4^{25}$  0.9470,  $n_D^{25}$  1.51385, is prepared by the addition of magnesium to a mixture of cuminaldehyde,  $C_6H_5Pr^o\text{-CHO}$ , and  $\alpha$ -bromoallene. The carbinol on oxidation with potassium permanganate yields a mixture of  $\beta$ -hydroxy- $\beta$ -cumylpropionic and  $p$ -isopropylcinnamic acids.

R. T.

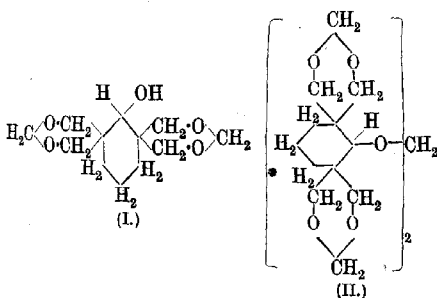
**Synthesis of Keto-alcohols and Polyhydroxy-alcohols from Cyclic Ketones and Formaldehyde.** C. MANNICH and W. BROSE (*Ber.*, 1923, 56, [B], 833—844).—Tollens's method for the production of polyhydroxy-alcohols by the action of an excess of formaldehyde on aliphatic aldehydes and ketones in the presence of milk of lime has been extended to cyclic ketones, including cyclohexanone, *o*- and *p*-methylcyclohexanones, cyclopentanone, menthone, carvone, and camphor. With the three substances last mentioned, a condensation could not be effected. In the case of cyclohexanone and its *o*- and *p*-methyl derivatives, the action follows the expected course, two hydroxymethyl groups being introduced at each carbon atom vicinal to the ketonic group and the latter suffering reduction to the secondary alcoholic group when excess of formaldehyde is employed. When smaller quantities of the latter are taken it is possible to control the action in such a manner that keto-alcohols are produced. With cyclopentanone, on the other hand, the reaction follows a rather different course, yielding either condensation products of high molecular weight or a tetrahydroxy-keto-alcohol according to the proportion of formaldehyde employed.

2 : 2 : 6 : 6-Tetrahydroxymethylcyclohexane-1-ol,



colourless, quadratic plates, m. p. 131° (corr.), is prepared by allowing a homogeneous mixture of cyclohexanone, formaldehyde, and water to remain in contact with slaked lime at 30° during several days. It gives a *penta-acetate*, needles, m. p. 75° (corr.). It is converted by formaldehyde (30%) and concentrated hydro-

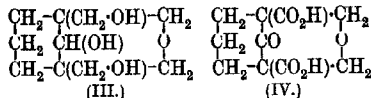
chloric acid into a mixture of the *bismethylene ether* (annexed formula I), colourless plates, m. p. 119° (corr.) [corresponding *monoacetate*, pointed rhombs, m. p. 135° (corr.)],



and the compound (annexed formula II), colourless, lustrous leaflets,

x\*

m. p. 242° (corr.). Hydrogen chloride at 150—160° converts 2:2:6:6-tetrahydroxy-methylcyclohexane-1-ol into the cyclic ether (annexed formula III), colourless crystals, m. p. 144° (corr.) [correspond-



ing triacetate, colourless plates, m. p. 72° (corr.)], which is oxidised by concentrated nitric acid to the dicarboxylic *keto-acid* (annexed formula IV), colourless needles, m. p. 218° (corr.). The latter substance is converted by phenylhydrazine into the compound,  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$ , small, colourless needles, m. p. 251° (corr.).

*cyclohexanone* is converted by four molecular proportions of formaldehyde into 2:2:6:6-tetrahydroxymethylcyclohexane-1-one, colourless, four-sided, double pyramids, m. p. 143° (corr.) [corresponding *tetra-acetate*, colourless prisms, m. p. 140° (corr.)]. The presence of the ketonic group cannot be established directly, since the compound could not be caused to react with phenylhydrazine, semicarbazide, or hydroxylamine, and the possibility of a cyclic structure is therefore not excluded. Indirectly, however, this can be effected, since the corresponding *bismethylene ether*, colourless prisms, m. p. 150° (corr.), is reduced by alcohol and a large excess of sodium to the bismethylene ether of tetrahydroxymethylcyclohexanol which is identical with the product (formula I) described above. The *bisbenzylidene ether* of 2:2:6:6-tetrahydroxymethylcyclohexane-1-one, long, colourless needles, m. p. 230·5° (corr.), is readily prepared from the parent substance, benzaldehyde, and hydrochloric acid and is resolved into its components by treatment with boiling mineral acid.

2-Hydroxymethylcyclohexane-1-one is prepared from equimolecular proportions of *cyclohexanone* and formaldehyde. It is a colourless liquid, b. p. 114—115°/16 mm., which is sensitive towards both acids and alkalis. It gives a *monoacetate*, a colourless liquid, b. p. 134—136°/15 mm. (prepared by the aid of acetyl chloride in the presence of pyridine), and a *phenylhydrazone*, small, colourless prisms, m. p. 129°.

*p*-Methylcyclohexanone and formaldehyde (5·5 molecular proportions) give 4-methyl-2:2:6:6-tetrahydroxymethylcyclohexane-1-ol, small, colourless needles, m. p. 150° (corr.), which is further characterised by its conversion by acetic anhydride and sodium acetate into the *penta-acetate*, leaflets, m. p. 139° (corr.).

The product obtained by the similar condensation of *o*-methylcyclohexanone with formaldehyde could not be caused to crystallise, and was therefore treated with benzaldehyde and concentrated hydrochloric acid, whereby the *bisbenzylidene ether* of 2-methyl-2:6:6-trihydroxymethylcyclohexane-1-ol was obtained in colourless prisms, m. p. 133° (corr.). Treatment of the ether with hot aqueous hydrochloric acid leads to the production of 2-methyl-2:6:6-trihydroxymethylcyclohexane-1-ol, short, colourless prisms, m. p. 100° (corr.).

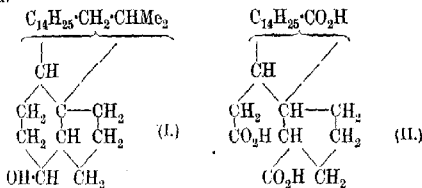
Treatment of *cyclopentanone* with a large excess of formaldehyde

and slaked lime causes the slow formation of insoluble, amorphous condensation products. With 4-6 molecular proportions of aldehyde and moderate quantities of slaked lime, 2:2:5:5-tetrahydroxymethylcyclopentane-1-one, colourless plates, m. p. 143° (corr.), is produced. The presence of four hydroxy-groups is established by the isolation of a tetrabenzoate, colourless needles, m. p. 144° (corr.). The compound, however, does not appear to react with phenylhydrazine, semicarbazide, hydroxylamine, or hydrogen cyanide; attempts to reduce it to the corresponding secondary alcohol were unsuccessful. It yields a bismethylene ether, m. p. 182° (corr.), and a bisbenzylidene ether, long, colourless needles, m. p. 206.5° (corr.). The bismethylene ether is reduced by sodium and boiling alcohol to the bismethylene ether of 2:2:5:5-tetrahydroxymethylcyclopentane-1-ol, colourless plates, m. p. 81° (corr.), which gives a monoacetate, prisms, m. p. 106° (corr.).

H. W.

#### Conversion of Coprosterol into isoLithobilianic Acid. A.

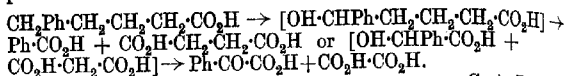
INDAUS and TH. RIEMANN (*Z. physiol. Chem.*, 1923, 126, 277-30).—Coprosterol, (I), when oxidised yields an acid,  $C_{27}H_{46}O_4$ ; it is now shown that this acid on further oxidation yields isoLithobilianic acid, (II), m. p. 262° (dimethyl ester, m. p. 204°), and the constitution assigned to these substances has thus been confirmed.



W. O. K.

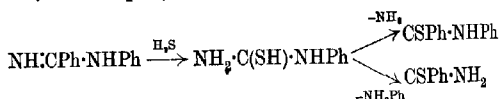
The Oxidising Action of Alkaline Potassium Permanganate on Normal Phenyl-fatty Acids. EUGENI STEPANOVITSCH PESHEVALSKI (*J. Russ. Phys. Chem. Soc.*, 1917-1918, 49, 57-572).—The oxidation of phenylated fatty acids in the animal organism has been shown by Dakin (A., 1908, ii, 964; 1910, ii, 795) and by Knoop (A., 1905, ii, 46) to take place at the  $\beta$ -carbon atom. It is now shown that hot alkaline permanganate in all cases attacks the carbon atom next to the phenyl group, a hydroxyl group being introduced; this may then be further oxidised to a keto- and finally to a carboxyl-group, forming benzoic acid; the remainder of the side-chain is oxidised to carbon dioxide or a dibasic acid. On the other hand, after the entrance of the first hydroxyl group into the molecule, the next carbon atom may be attacked and oxidised to carboxyl, forming a hydroxy- or keto-acid (mandelic or phenylglyoxylic acid), the remainder of the side-chain being oxidised to carbon dioxide or a dibasic acid. Thus, phenylacetic

acid yields benzoic and phenylglyoxylic acids; phenylpropionic acid gives mainly mandelic acid, also some benzoic and oxalic acid; the latter are the main products from phenylbutyric acid, in addition to some phenylglyoxylic acid; phenylvaleric acid gives the same three products in addition to succinic acid. The oxidation of phenylvaleric acid is thus an illustration of both the suggested processes:

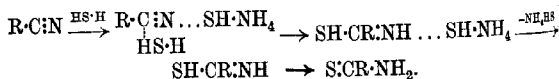


G. A. R. K.

**The Mechanism of Chemical Reactions. I. Reduction of Amides and Oxidation of Amines.** KARL KINDLER [and, in part, F. BURGHARD, F. FINNDORF, W. DEHN, O. GIESE, and P. KÖRDING] (*Annalen*, 1923, 431, 187—230).—It is already known that the addition of hydrogen sulphide to a nitrile group which is not attached to a negative residue (Ph or CN) cannot be effected unless ammonium hydrogen sulphide is present (Bernthsen, A., 1877, i, 616). This is not due to the intermediate production of an amidine:  $\text{R}\cdot\text{C}\cdot\text{N} \xrightarrow{+\text{NH}_3} \text{NH}\cdot\text{CR}\cdot\text{NH}_2 \xrightarrow{\text{H}_2\text{S}} \text{NH}_3 + \text{S}\cdot\text{CR}\cdot\text{NH}_2$ , because the action of alcoholic hydrogen sulphide, saturated at  $-10^\circ$ , on benzonitrile and dimethylamine at  $80-90^\circ$  leads only to the formation of thiobenzamide in 100% yield; if the reaction proceeded according to the above scheme, an *N*-alkylthioamide would also be produced, since hydrogen sulphide acts on phenylbenzylamine, for example (Bernthsen, A., 1878, 788), as follows:



The promotion of this reaction by means of ammonium hydrogen sulphide is therefore considered to be due to the intermediate formation of molecular compounds:



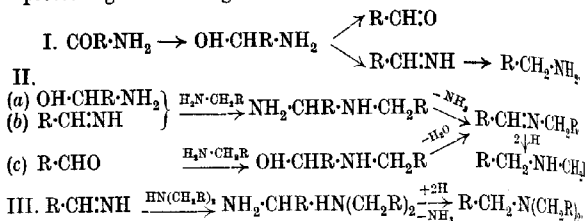
This view is confirmed by the fact that alkali hydrogen sulphides are even more efficient catalysts than ammonium hydrogen sulphide. Thus benzyl cyanide, heated for one and a half days at  $70^\circ$  with alcoholic hydrogen sulphide saturated at  $-10^\circ$ , does not give phenylthioacetamide, but if ammonia, dimethylamine, sodium hydroxide, or potassium hydroxide is added, the yield of this amide is 77, 81, 89, and 91%, respectively. The conversion is seldom quantitative, because the reaction is reversible; the same equilibrium:  $\text{RCN} + \text{H}_2\text{S} \rightleftharpoons \text{R}\cdot\text{CS}\cdot\text{NH}_2$  (89% theory) is attained in the presence of alcoholic sodium hydrogen sulphide, starting

from phenylthioacetamide. In the presence of alkali hydrogen sulphide or dimethylammonium hydrogen sulphide in dry benzene solution, the following thioamides are prepared from the relevant nitriles in the yields stated. Thioacetamide, 66%; thiopropionamide, 43%; thio-*p*-toluamide, 78%; thio- $\beta$ -naphthoamide, 88%; phenylthioacetamide, 83%; thioamide of acetylmandelic acid,  $\text{CO}_2\text{Me}\cdot\text{CHPh}\cdot\text{CS}\cdot\text{NH}_2$ , 70%; phenylthiopropionamide, m. p. 87°, 84%. Aliphatic and aliphatic-aromatic selenoamides are produced in the same way. Phenylacetoneitrile reacts at 80° with alcoholic hydrogen selenide, saturated at -10°, containing sodium hydrogen selenide, giving an almost quantitative yield of phenylselenoacetamide, glistening, white crystals, m. p. 92—92.5°; selenoacetamide, m. p. 126—126.5°, is obtained in the same way, yield 17%, from acetoneitrile.

The action of phosphorus pentasulphide on amides (Hofmann, A., 1878, 396) occurs in two stages. If the reaction is conducted in cold carbon disulphide solution, using *N*-dimethylbenzamide, the only additive product,  $\text{NH}_2\cdot\text{CR}\cdot\text{O}\dots(\text{S}_2)\text{P}\cdot\text{S}\cdot\text{P}(\text{S}_2)\dots\text{O}\cdot\text{C}(\text{NH}_2)\text{R}$  (cf. Pfeiffer, *Organischer Molekülverbindungen*, 1922, 156), may be isolated. This is decomposed by means of water into the amide, phosphoric acid, and hydrogen sulphide, but gives thiobenzodimethylamide, m. p. 67° (corr.), b. p. 180—182°/18 mm., in 93% yield, on being repeatedly extracted by means of warm xylene. The formation of the thioamide is considered to take place by an interchange of oxygen and sulphur atoms in the additive compound, followed by dissociation. The following thioamides are formed with especial readiness in the presence of potassium sulphide. Thioacetamide, 75%; phenylthioacetamide, 48%; phenylthiopropionamide, 45%; *N*-methylthiobenzamide, 78%; phenylthioacetothylamide, colourless plates, m. p. 62.5—63° (corr.), 75%; phenylthioacetodimethylamide, colourless crystals, m. p. 80—81° (corr.), 80%;  $\beta$ -phenylthiopropionodimethylamide, red oil, 83%.

The reduction of phenylacetamide by means of sodium and methyl alcohol leads to the formation, not only of  $\beta$ -phenylethylamine, but also of di-( $\beta$ -phenylethyl)amine. Moreover, secondary and even tertiary amines are produced when thioamides are reduced by means of aluminium amalgam in moist ethereal or alcoholic solution. Thus in ethereal solution the following amines are formed from the corresponding thioamides. 88% Benzylamine, 7% dibenzylamine, and traces of tribenzylamine. 84% *p*-Methylbenzylamine, 15% di-(*p*-methylbenzyl)amine. 26%  $\beta$ -Phenylethylamine, 66% di-( $\beta$ -phenylethyl)amine. 35%  $\gamma$ -Phenylpropylamine, 15% di-( $\gamma$ -phenylpropyl)amine,  $(\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{NH}$ , b. p. 245°/35 mm., hydrochloride, m. p. 203° (corr.) (cf. Rupe and Glenz, this vol., i, 100). In alcoholic solution, 69% benzylamine, 21% dibenzylamine, and traces of tribenzylamine; 74% *p*-methylbenzylamine, 15% secondary amine; 22%  $\beta$ -phenylethylamine, and 21% secondary amine are produced. To explain these results, the intermediate formation of an aminoalcohol,  $\text{OH}\cdot\text{CHR}\cdot\text{NH}_2$ , or aminothioalcohol,  $\text{SH}\cdot\text{CHR}\cdot\text{NH}_2$ , is postulated, the production of primary, secondary, or tertiary amine from an amide being then

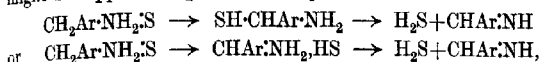
expressed by the following scheme, the reduction of a thioamide proceeding in an analogous manner :



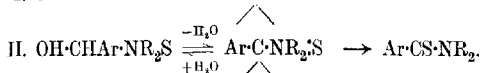
In accordance with this explanation, secondary and tertiary amines are not formed in acid solution; the aminothio-alcohol, being unstable to acids, undergoes fission to an aldehyde or to an aldimine, the latter being further reduced to a primary amine. Thus the electrolytic reduction of phenylthioacetamide in alcoholic hydrogen chloride solution leads to a 63% yield of  $\beta$ -phenylethylamine, and the reduction of thiobenzamide in dilute acetic acid solution by means of iron powder in an atmosphere of carbon dioxide gives benzaldehyde in a yield corresponding quantitatively with the amount of unrecovered thioamide. Moreover, the reduction of phenylthioacetamide by means of aluminium amalgam in moist ethereal solution containing ethylamine gives  $\beta$ -phenylethylamine, di-( $\beta$ -phenylethyl)amine, and  $\beta$ -phenylethylethylamine, *hydrochloride*, whilst  $\beta$ -phenylethyldimethylamine is formed in the presence of dimethylamine. *N*-Monoalkyl or dialkyl amides or thioamides also pass first into the aminoalcohol or aminothioalcohol. Hence the electrolytic reduction of thiobenzanilide in 80% sulphuric acid solution at 15–20°, using a current density 0.15 amp./sq. cm., gives about 10% benzalaniline besides considerable amounts of aniline and benzaldehyde, whilst under similar conditions *N*-benzothiodimethylamide gives benzyldimethylamine, dimethylamine, and about 40% benzaldehyde. The preparation of tertiary amines from thiodialkylamides may, however, be accomplished by reduction in 60% sulphuric acid solution, using a current density 0.3 amp./sq. cm. Thiobenzodimethylamide, phenylthioacetodimethylamide, and  $\beta$ -phenylthiopropionodimethylamide give, respectively, benzyldimethylamine, 100%,  $\beta$ -phenylethyldimethylamine, 100%, and  $\gamma$ -phenylpropyldimethylamine, 73%. Benzylmethylamine, *p*-methoxybenzylmethylamine, and  $\beta$ -phenylethylmethylamine are obtained in yields of 79, 84, and 83%, respectively, by the reduction of the corresponding thioamides in concentrated hydrochloric acid solution. The reduction by means of aluminium amalgam of thioacetanilide, in ethereal solution, of thiobenzomethylamide, and of thiobenzodimethylamide, in alcoholic solution, gives ethylamine, 100%, benzylmethylamine, 70%, and benzyldimethylamine, 60%, respectively.

Benzylamine is oxidised to benzamide by means of cold alkaline potassium permanganate (cf. Bamberger and Scheutz, A., 1901

i, 587), but at 100° only benzoic acid and ammonia are produced; hence benzaldoxime is not an intermediate product. The parallel conversion of amines into thioamides by heating with sulphur (Wallach, A., 1891, 189) proceeds more readily, but has only been accomplished in the arylmethylamine series. Hence the reaction might be supposed to proceed through an aldimine:

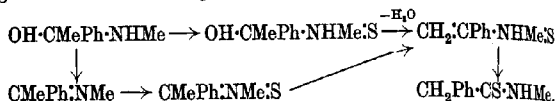


but for the fact that tertiary amines, which cannot be converted into aldimines, undergo this reaction. Thus benzyldimethylamine gives thiobenzodimethylamide when heated for four hours at 180° with sulphur (2 atoms). That in the oxidation of amines an amino-alcohol is primarily formed is supported by the fact (Pickard and Carter, T., 1901, 79, 520) that amino-alcohols can be oxidised to amides; moreover, both amino-alcohols and aminothio-alcohols may be converted into thioamides by heating with sulphur (see below). This is not merely dehydrogenation:  $\text{OH}\cdot\text{CHR}\cdot\text{NR}_2 + \text{S} = \text{R}\cdot\text{CO}\cdot\text{NR}_2 + \text{H}_2\text{S}$ , since the corresponding amides do not react with sulphur under similar conditions. Indeed, whether the amino-alcohol or the aldimine is the intermediate product, the formation of a compound of bivalent carbon must be postulated:



The aldehyde or ketone and ammonia or the amine are mixed in equivalent proportions, with cooling, and the mixture is heated with sulphur for three hours at 170–180°. Benzaldehyde and ammonia give thiobenzamide. *p*-Tolualdehyde and methylamine give *thio-p-tolumethylamide*, m. p. 55°. Benzaldehyde and  $\beta$ -naphthylamine give *thiobenzo- $\beta$ -naphthylamide*, m. p. 106–107°. Benzaldehyde and dimethylamine give thiobenzodimethylamide; benzaldehyde and diethylamine give *thiobenzodiethylamide*, b. p. 194°/18 mm. Anisaldehyde and dimethylamine give *thio-p-methoxybenzodimethylamide*, m. p. 68.5°. Phenylacetaldehyde and dimethylamine give phenylthioacetodimethylamide. Similar compounds are produced by the action of sulphur on aldimines and ketimines; these are prepared by heating an equimolecular mixture of a primary amine and an aldehyde or ketone at 80–90° for three to four hours, and distilling the product under reduced pressure. Benzyldimethylamine gives *N*-methylthiobenzamide. *p*-Methoxybenzylidenemethylamine,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NMe}$ , b. p. 129–130°/18 mm., gives *p*-methoxythiobenzomethylamide, m. p. 108–109°. Benzyldiene-aniline gives thiobenzanilide and  $\alpha$ -phenylethylidenemethylamine,  $\text{CMePh}\cdot\text{NMe}$ , b. p. 96°/10 mm., gives phenylthioacetomethylamide. Phenylthioacetodimethylamide is produced when acetophenone and dimethylamine are heated with sulphur. Similarly, *p*-acetylanisole and dimethylamine give *p*-methoxyphenylthioacetodimethyl-

amide, m. p. 75—76°, whilst the products when diethylamine is used are, respectively, *phenylthioacetodiethylamide*, b. p. 184°/12 mm., and *p-anisylthioacetodiethylamide*, b. p. 220°/12 mm. In these reactions, the migration of an alkyl group must occur. It is suggested that the intermediate hydramine or ketimine forms an amine sulphide; this is followed by dehydration or migration of a hydrogen atom, giving an ethylene derivative, which then undergoes molecular rearrangement to the thioamide:



It is indicated that amino-alcohols may be intermediate products in the interconversion of amines and amides in plants and animals.

Use is made of thioamides in the synthesis of hordenine and hydrastinine. *p*-Nitrophenylacetodimethylamide, when treated with phosphorus pentasulphide and potassium sulphide, gives *p*-nitrophenylthioacetodimethylamide, yellowish-green prisms or leaflets, m. p. 131° (corr.), yield 90%, which on electrolytic reduction in 60% sulphuric acid solution gives *p*-amino- $\beta$ -phenylethylmethylamine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , colourless crystals, m. p. 40—42° (corr.), b. p. 137—138°/6 mm., *hydrochloride*, m. p. 261° (corr.). By diazotisation and warming in aqueous solution, hordenine is obtained in 95% yield. When the *N*-methylammonium salt of homopiperonylic acid is heated at 185—195° for two hours in an atmosphere of methylamine, an 85% yield of homopiperonylmethylamide, m. p. 106° (corr.), is obtained. This is treated with phosphorus pentasulphide and potassium sulphide, giving homopiperonylthiomethylamide, m. p. 136° (corr.), yield 82%, which is converted by electrolytic reduction in alcoholic hydrochloric acid solution into piperonylmethylamine, yield 80%, from which hydrastinine is obtained by the method of Decker and Becker (A., 1913, i, 290).

W. S. N.

**The Resolution of *p*- and *m*-Nitrophenoxypropionic Acids.**  
E. FOURNEAU and G. SANDULESCO (*Bull. Soc. chim.*, 1923, [iv], 33, 459—465).—The resolution of *o*-nitrophenoxypropionic acid by means of cinchonine, strychnine, and yohimbine has already been described (*loc. cit.*, 1922, 31, 988), but the methods which were successful with the ortho-acid do not give uniformly good results with the meta- and para-acids. The cinchonine and cinchonidine salts of the para-acid are oily or gummy and fail to crystallise, whilst the crystallisation of the strychnine and brucine salts is good, but no resolution occurs. On the other hand, *L*-*p*-nitrophenoxypropionic acid was obtained in good yield by the fractional crystallisation of the yohimbine salt. It melts at 89—90° and has  $[\alpha]_D -53.7^\circ$ . The *d*-acid was obtained by means of the quinidine salt. For the resolution of the meta-acid strychnine gave the best results amongst the various alkaloids tried. The salt of the *l*-acid crystallised out, and had a constant rotation after three

recrystallisations,  $[\alpha]_D -25^\circ$ . The free *l*-nitrophenoxypionic acid had m. p.  $101-102^\circ$ , and  $[\alpha]_D -51.87^\circ$ . G. F. M.

**Researches on Residual Affinity and Co-ordination. XVI. Normal and Acid Salicylatotetramminocobaltic Salts.** GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1923, 123, 1096-1108).

**Silver Derivative of Amino-thiolbenzoic Acid.** A. FELDT (U.S. Pat. 1439624).—Interaction of a silver salt, in particular silver nitrate, with 4-amino-2-thiolbenzoic acid yields the compound,  $\text{AgS}\cdot\text{C}_6\text{H}_4(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , a colourless powder, m. p.  $205^\circ$ .

## CHEMICAL ABSTRACTS.

**Oxalic Acid Derivatives of Benzo- and *p*-Tolu-acetodinitriles.** ERICH BENARY, HELENE SOENDEROP, and ERICH BENNEWITZ (Ber., 1923, 56, [B], 910-917).—A continuation of previous work (cf. Benary and Schmidt, A., 1921, i, 776).

*Ethyl  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -phenylbutyrate*,  $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , lustrous plates, decomp.  $165-167^\circ$ , is prepared by the action of benzoacetodinitrile, ethoxalyl chloride, and pyridine in the presence of anhydrous ether. (The substance described under this name by von Meyer [A., 1914, i, 999] is actually the corresponding *N*-derivative.) It is converted by phenylhydrazine in acetic acid solution (50%) into 4-cyano-1:3-diphenylpyrazole-5-carboxyphenylhydrazide,  $\text{Ph}\overset{\text{C}}{\underset{\text{N}-\text{NPh}}{\text{C}}}(\text{CN})\gg\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , needles, m. p.  $215-216^\circ$ , which is

converted by prolonged treatment with *N*-sodium hydroxide solution into 4-carbamido-1:3-diphenylpyrazole-5-carboxyphenylhydrazide, m. p.  $269^\circ$ . The cyano-compound is oxidised by potassium permanganate in the presence of acetone to 4-cyano-1:3-diphenylpyrazole-5-carboxylic acid,  $\text{Ph}\overset{\text{C}}{\underset{\text{N}-\text{NPh}}{\text{C}}}(\text{CN})\gg\text{C}\cdot\text{CO}_2\text{H}$ , colourless needles,

m. p.  $216-217^\circ$  (decomp.), which is converted by sodium hydroxide solution (10%) into 1:3-diphenylpyrazole-4:5-dicarboxylic acid, m. p.  $197^\circ$  (decomp.). *Ethyl  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -phenylbutyrate* is transformed by alcoholic ammonia into the corresponding amide,  $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$ , lustrous leaflets, m. p.  $212-213^\circ$  (decomp.) after progressive decomposition above  $198^\circ$ , and by the calculated quantity of cold *N*-sodium hydroxide solution into the imino-lactone,  $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$ , lustrous, quadratic leaflets, m. p.  $272^\circ$  (decomp.). The latter substance is transformed by phenylhydrazine into the phenylhydrazide,

$\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ ,

matted needles, m. p.  $279-280^\circ$  (decomp.). *Ammonium  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -phenylbutyrate*, m. p.  $181-183^\circ$  (decomp.), was obtained in one instance from the products of the action of water at  $60-70^\circ$  on the ester and was converted into the copper salt, a dark green, voluminous precipitate from which  *$\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -phenylbutyric acid*, an unstable compound, m. p.  $132^\circ$  (decomp.), is isolated by the action of hydrogen sulphide in the presence of ether.

Benzoacetodinitrile is converted by oxalyl chloride in the presence of ether and pyridine into *oxalylbisbenzoacetodinitrile*,  $C_{26}H_{14}O_2N_4$ , m. p. 217—218° (decomp.).

*p*-Toluoacetodinitrile, ethoxalyl chloride, and pyridine in the presence of anhydrous ether give *ethyl  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -p-tolylbutyrate*,  $NH_2C(C_6H_4Me) \cdot CH(CN) \cdot CO \cdot CO_2Et$ , long, colourless needles, m. p. 132—133° (decomp.), which is converted by phenylhydrazine into *4-cyano-1-phenyl-3-p-tolylpyrazole-5-carboxyphenylhydrazide*,  $C_{24}H_{19}ON_5$ , lustrous needles, m. p. 224—225°, and *4-carbamido-1-phenyl-3-p-tolylpyrazole-5-carboxyphenylhydrazide*,  $C_{24}H_{21}O_2N_5$ , small needles, m. p. 266—268°. Oxidation of the cyanohydrazide by potassium permanganate in the presence of acetone leads to the formation of *4-cyano-1-phenyl-3-p-tolylpyrazole-5-carboxylic acid*, microscopic needles, m. p. 208—209°. Ethyl  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -p-tolylbutyrate is converted by alcoholic ammonia into  *$\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -p-tolylbutyramide*, m. p. 195—196° (decomp.) after darkening and incipient decomposition at 175°, and by *N*-sodium hydroxide solution into the *imino-lactone*,  $C_{12}H_{10}O_3N_2$ , slender needles, decomp. 301°. Ammonium  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -keto- $\gamma$ -p-tolylbutyrate, m. p. 165—166° (decomp.), is obtained as in the case of the corresponding phenyl compound and is similarly transformed into the *copper* salt and the *free acid*, m. p. 149° (decomp.).

The compounds obtained by von Meyer (*loc. cit.*) from *p*-toluoacetodinitrile are to be regarded as *N*-derivatives.

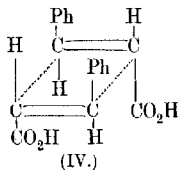
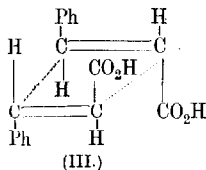
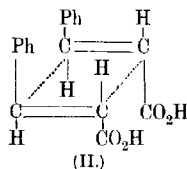
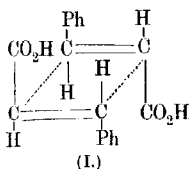
*C-Oxalylbisdiacetodinitrile*,  $C_{10}H_{10}O_2N_4$ , four-sided prisms which slowly become carbonised above 195°, is obtained from diacetodinitrile, pyridine, and oxalyl chloride in the presence of anhydrous ether.  
H. W.

**The Constitution of the Truxillic and Truxinic Acids and the Action of Sunlight on the Cinnamic Acids and their Salts.**  
A. W. K. DE JONG (*Ber.*, 1923, **56**, [B], 818—832).—The action of sunlight on the normal and acid salts of *trans*-cinnamic acid has been investigated, the material being spread evenly over glass plates placed in shallow wooden boxes and not further covered. Under these conditions, lithium *trans*-cinnamate gives  $\beta$ - and  $\epsilon$ -truxinic acids, the sodium and potassium salts yield only  $\beta$ -truxinic acid, whereas methyl *trans*-cinnamate gives  $\alpha$ -truxillic acid. Among salts of the bivalent metals, the stable strontium salt and the copper, cadmium, manganese, ferrous, and cobaltous salts do not give truxillic and truxinic acids.  $\beta$ -Truxinic acid is exclusively obtained from the magnesium and nickel salts and from the barium salt after desiccation at 100°. The metastable strontium and the stable barium salts yield  $\beta$ -truxinic and  $\epsilon$ -truxillic acids, whereas the metastable barium and the stable lead salts give  $\beta$ - and  $\delta$ -truxinic acids.  $\delta$ -Truxinic acid in large amount and only a small quantity of  $\beta$ -truxinic acid are obtained from the metastable lead salt, so that it does not appear improbable that the occurrence of the  $\beta$ -acid is due to the partial transformation of the salt into the stable form. Exclusive production of  $\epsilon$ -truxillic acid is not observed.

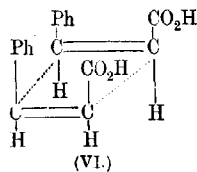
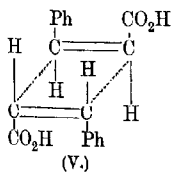
The strontium and barium salts after being heated during eight days do not yield  $\alpha$ -truxillic acid when illuminated; truxinic or truxillic acids are not obtained from the double salt derived from calcium benzoate and calcium *trans*-cinnamate.

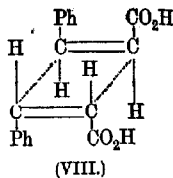
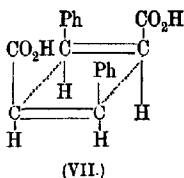
Among the hydrogen salts, the lithium and ammonium compounds yield  $\beta$ -truxinic and  $\alpha$ -truxillic acids; the production of the latter acid is probably due to the salts becoming moist and sticky, and thus converted into a mixture of free acid and normal salt.  $\beta$ -Truxinic acid is alone obtained from the strontium and barium compounds. The sodium and caesium salts yield  $\beta$ - and  $\delta$ -truxinic acids, whereas  $\beta$ -truxinic and  $\epsilon$ -truxillic acids are derived from the potassium compound.

The author seeks an explanation of the polymerisation of the cinnamic acids in the hypothesis that the cinnamic acid molecules are held by the partial valencies of the double bond in such a manner that the latter are always parallel to one another. In the case of the *trans*-cinnamic acid four possibilities present themselves as shown by the formulæ



The production of  $\alpha$ -truxillic (I),  $\beta$ -truxinic (II),  $\epsilon$ -truxillic, (III) and  $\delta$ -truxinic (IV) acids is thus readily explained. Considerations of symmetry show this property to decrease in the given sequence and the stability must consequently diminish in the same order. This is in good accord with the known properties of the  $\alpha$ - and  $\beta$ -cinnamic acids, and the non-occurrence of the other two possible forms. Similarly, four forms are possible for the *cis*-cinnamic acids as shown in the scheme :





The symmetry and consequently the stability diminish in the given order. The formulæ V, VI, and VII represent, therefore, the nuclei of the acids, m. p. 68°, 58°, and 42°, respectively.

Illumination of the normal calcium salt gives  $\beta$ -truxinic acid and a new acid, m. p. 214°, which is only formed in very small quantity.

The following salts of cinnamic acid are described. The normal strontium compound crystallises when its aqueous solution is rapidly cooled in small, metastable needles which rapidly pass in contact with the solution into larger needles of the stable salt. Similarly, metastable *barium* cinnamate ( $+2\text{H}_2\text{O}$ ) crystallises in lustrous, thin, hexagonal leaflets from its highly concentrated solution which pass into small needles of the stable form. The metastable form of lead cinnamate, small needles, is converted more slowly into the stable modification.

The following acid salts have not been described previously. They are all anhydrous. The *lithium* salt,  $\text{C}_9\text{H}_7\text{O}_2\text{Li}\cdot\text{C}_6\text{H}_5\text{O}_2$ , the *rubidium*, *cæsium*, *strontium*, and *barium* salts. The corresponding calcium salt could not be prepared. For the purposes of comparison, the following benzoates have been prepared; the *barium* salt,  $(\text{Ph}\cdot\text{CO}_2)_2\text{Ba}\cdot 2\text{Ph}\cdot\text{CO}_2\text{H}$ , small, slender needles; the *strontium* salt,  $(\text{Ph}\cdot\text{CO}_2)_2\text{Sr}\cdot\text{Ph}\cdot\text{CO}_2\text{H}$ , slender needles; the *calcium* salt,  $(\text{Ph}\cdot\text{CO}_2)_2\text{Ca}\cdot\text{Ph}\cdot\text{CO}_2\text{H}$ . The ratio of acid to normal salt is not affected in the two latter instances by the presence of an excess of acid.

H. W.

**The Dinaphthanthracene Series. V.** ERNST PHILIPPI and REINHARD SEKA [with MOLLY HAUSENBICHL] (*Monatsh.*, 1923, 43, 615—619; cf. A., 1921, i, 728).—Pyromellitic anhydride readily condenses with *p*-xylene at 75° in presence of aluminium chloride to give a mixture of 4:6-*di-p*-xylylisophthalic and 2:5-*di-p*-xylyltetraphthalic acids. The recrystallised mixture (m. p. 298°) is converted by concentrated sulphuric acid into 1:4:8:11-tetramethyl-5:7:12:14-dinaphthanthradiquinone, greenish-yellow needles, darkening at 340° and charring at 385° without melting. This substance does not give a vat colour with alkali hyposulphite, but on oxidation with nitric acid passes into 5:7:12:14-dinaphthanthradiquinone-1:4:8:11-tetracarboxylic acid (darkening at 250° and charring at 325°), which dyes cotton pale rose-red shades and, with hyposulphite, affords a deep red vat colour, the latter becoming blue in presence of alkali (cf. Seer, A., 1912, i, 571).

E. E. T.

**The Dinaphthanthracene Series. VI. ERNST PHILIPPI and REINHARD SEKA** [with WILHELM FIGDOR and RUDOLF NEMECZEK] (*Monatsh.*, 1923, **43**, 821—831; cf. preceding abstract, and Fairbourn, T., 1921, **119**, 1573).—Pyromellitic anhydride condenses with *o*-xylene in presence of aluminium chloride to give a mixture of 4:6-di-*mp*-dimethylbenzoylisophthalic and 2:5-di-*mp*-dimethylbenzoylterephthalic acids, separable into a sparingly soluble acid (m. p. 312°) and a soluble acid (m. p. 250°). The corresponding mixture of acid chlorides loses hydrogen chloride when treated with aluminium chloride, but no isolable compound results.

Pyromellitic anhydride and anisole condense to give a mixture (m. p. 200—250°) of 4:6-di-*p*-methoxybenzoylisophthalic and 2:5-di-*p*-methoxybenzoylterephthalic acids, which may be separated by crystallisation from water. The 2:5-acid (sparingly soluble) melts at 311°, the 4:6-acid (more soluble) at 285°, with previous discoloration. Neither acid is convertible by means of sulphuric acid into a dinaphthanthradiquinone.

Pyromellitic anhydride condenses with quinol dimethyl ether to give a poor yield of the two expected di-2:4-dimethoxybenzoylisophthalic and -terephthalic acids (green product, m. p. about 220°).

Anthracene-2:3-dicarboxylic anhydride and benzene on condensation give an ill-defined product, melting indefinitely at 130°, and giving, on oxidation, 2-benzoylanthraquinone-3-carboxylic acid, m. p. (indef.) 275°. Magnesium phenyl bromide converts anthracene-dicarboxylic anhydride into the corresponding diphenylphthalide derivative (yellow, m. p. 260°), and this, on oxidation, gives the corresponding anthraquinone derivative (yellow, m. p. 200°).

Bromination of dinaphthanthradiquinone at 300° gives a mixture of products, of which the isolable one is a dibromo-derivative, sintering at 358° and melting at 363°. Nitration of the diquinone gives a dinitro-derivative, darkening and charring at 380—400°. E. E. T.

**The Symmetric and Mixed Esters of Carboxycamphoracetic Acid and their Saponification Products.** A. HALLER and L. PALFRAY (*Compt. rend.*, 1923, **176**, 1193—1197).—The following esters of carboxycamphoracetic acid having the general

formula  $C_8H_{14} \begin{smallmatrix} \diagup \\ C(CO_2R')-CH_2-CO_2R \\ \diagdown \\ CO \end{smallmatrix}$  were prepared in the manner

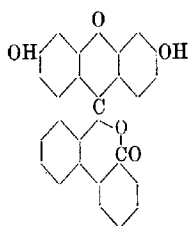
previously described (A., 1905, i, 601) by the action of the corresponding iodoacetic ester on the sodium camphorcarboxylic ester:—Diethyl ester, b. p. 199—200°/14 mm.,  $[\alpha]_D + 59.43^\circ$ ; phenyl(R)-methyl(R') ester, b. p. 233—235°/13 mm., m. p. 83°,  $[\alpha]_D + 41.38^\circ$ ; benzyl(R')methyl(R) ester, b. p. 265—270°/16 mm.,  $[\alpha]_D + 46.1^\circ$ . On saponification by alkalis or mineral acids, only the acetic ester (R) group is removed provided the temperature is kept below 150°, the carboxylic ester (R') group proving exceptionally stable. The above-mentioned diethyl ester furnishes therefore a carboxycamphoracetic acid of the constitution  $C_8H_{14} \begin{smallmatrix} \diagup \\ C(CO_2Et)-CH_2-CO_2H \\ \diagdown \\ CO \end{smallmatrix}$ ;

forming large crystals, m. p. 117—118°. The dimethyl ester similarly gives the corresponding monomethyl ester, m. p. 177—178°,

and the above phenyl methyl ester gives the same product. The benzyl methyl ester gives the benzylcarboxylate, which forms an uncrystallisable oil. The action of hydrochloric acid on the esters at 180–190° under pressure effects the hydrolysis of both ester groups with simultaneous elimination of carbon dioxide and forma-

tion of *camphoracetic acid*,  $C_8H_4 \begin{smallmatrix} \text{CH-CH}_2\text{-CO}_2\text{H} \\ \text{CO} \end{smallmatrix}$ , m. p. 84–86°,  $[\alpha]_D + 72.35^\circ$ . G. F. M.

#### Condensation of Diphenic Anhydride with Resorcinol.



FRITZ BISCHOFF and HOMER ADKINS (*J. Amer. Chem. Soc.*, 1923, 45, 1030–1033).—Diphenic anhydride and resorcinol are condensed by heating at 135–150° with zinc chloride, to give the 9-lactone of 2'-(3'' : 6'' : 9''-trihydroxyanthracyl)diphenyl-2-carboxylic acid (annexed formula), an amorphous, ruby-red glass, which reacts with bromine in alcoholic solution to give the corresponding 2'' : 4'' : 5'' : 7''-tetrabromo-derivative, a pinkish-yellow solid. Both these compounds give acetylated

products which are insoluble in alkalis.

W. S. N.

**The Sodium Salts of Phenolphthalein.** HENRY BASSETT and PHILIP HALTON (*T.*, 1923, 123, 1291–1304).

**The Molecular Configurations of Polynuclear Aromatic Compounds.** III. **Diphenyl-3 : 5 : 3' : 5'-tetracarboxylic Acid.** HAROLD BURTON and JAMES KENNER (*T.*, 1923, 123, 1043–1045).

**Derivatives of 2 : 4-Dinitrobenzaldehyde.** III. THOMAS B. DOWNEY and ALEXANDER LOWY (*J. Amer. Chem. Soc.*, 1923, 45, 1060–1065; cf. *A.*, 1920, i, 440; 1921, i, 337).—A number of Schiff bases derived from 2 : 4-dinitrobenzaldehyde are described; the intermediate condensation product with *o*-tolidine is formed in a 95% aqueous alcoholic solution, but the Schiff base is produced in the presence of acetic acid. A number of triphenylmethane derivatives have been prepared by the condensation of 2 : 4-dinitrobenzaldehyde (1 mol.) with a tertiary alkylated aromatic amine or substituted aromatic amine or phenolic substance (2 mols.).

The additive compound of 2 : 4-dinitrobenzaldehyde and *o*-tolidine,  $C_6H_3(NO_2)_2 \cdot CH(OH) \cdot NH \cdot C_6H_3Me \cdot C_6H_3Me \cdot NH_2$ , deep purple plates, m. p. 232°, is converted by acetic acid in acetone solution into 2 : 4-dinitrobenzylidene-*o*-tolidine, yellowish-red crystals, m. p. 282° (decomp.), which reacts with acetic anhydride to give 2 : 4-dinitrobenzylideneacetyl-*o*-tolidine, orange-yellow needles, m. p. 231.5°. The following Schiff bases are also described: 2 : 4-dinitrobenzylidene-*o*-dichloroaniline,  $C_6H_3(NO_2)_2 \cdot CH : N \cdot C_6H_3Cl_2$ , bright orange plates, m. p. 185°; 2 : 4-dinitrobenzylidene-*o*-chloroaniline, yellow needles, m. p. 167.5°; 2 : 4-dinitrobenzylidene-*p*-chloroaniline, yellow needles, m. p. 161.5°; 2 : 4-dinitrobenzylidene-*p*-aminoazobenzene, red prisms, m. p. 229°. The following triphenylmethane derivatives

described: 2'' : 4''-dinitro-4 : 4'-dihydroxytriphenylmethane,  $H_3(NO_2)_2 \cdot CH(C_6H_4 \cdot OH)_2$ , pale yellow solid, m. p. 204°, which gives a tetrabromo-derivative, yellow needles, m. p. 234°; 4 : 4'-dinitro-2 : 4'-dinitrotriphenylmethane, m. p. 190.5°; op-dinitrophenyl-2 : 4'-cresolmethane, m. p. 200.5°; op-dinitrophenyl-di-guaiacolmethane, m. p. 221°; op-dinitrobenzylidenedi-4-salicylic acid, m. p. 138.5°, all of which are yellow solids. 2'' : 4''-Dinitro-4 : 4'-diethylaminotriphenylmethane, yellow needles, m. p. 151.5°; the corresponding bisdiethylamino-compound, an unstable, dirty green solid, and the benzylethylamino-compound, a brownish-yellow solid. The last three compounds give colour bases and dyes. The formation of op-dinitrophenyl-di-4'-resorcinolmethane, yellow, amorphous solid, chars above 280°, red calcium salt, is accompanied by the reduction of 3 : 6-dihydroxy-9-op-dinitrophenylxanthen, a yellowish solid, amorphous solid, which chars above 280°, which is also formed the condensation is carried out in the presence of zinc chloride at 5—130°, or of sulphuric acid at 60°; it yields a calcium salt and a tetrabromo-derivative, red prisms, decomp. 290° (cf. *J.S.C.I.*, 1923, 490A). W. S. N.

**The Isomerism of the Oximes. XI. Carbethoxy-derivatives.** OSCAR LISLE BRADY and GERALD PATRICK McHUGH *ibid.*, 1923, 123, 1190—1198).

**Peroxides of Monoximes.** R. CIUSA and E. PARISI (*Gazzetta*, 1923, 53, i, 143—149).—*m*-Nitrobenzaldoxime peroxide, obtained either by passing a slow current of nitrogen trioxide into an ethereal solution of the oxime or by oxidising the latter by means of amyl trite, has m. p. 131°, as stated by Ponzio (*A.*, 1906, i, 593), and at 105°, as given by Minunni and Ciusa (*A.*, 1906, i, 187), or 124°, as given by Franzen and Zimmermann (*A.*, 1906, i, 388). The action of nitrogen trioxide on the oxime dissolved in ether yields, in addition to the peroxide, (1) a substance, probably *m*-nitrobenzonitric acid,  $NO_2 \cdot C_6H_4 \cdot C(NO_2) \cdot N \cdot OH$ , which reddens sodium carbonate solution and is converted by this reagent into a mixture of di-*m*-nitrobenzildioxime peroxide, m. p. 184°, and 3 : 4-di-*m*-nitrophenylfurazan, m. p. 168°; (2) *m*-nitrobenzoic acid; (3) a compound, m. p. 147—150°, which is identical with that described by Bamberger and Scheutz (*A.*, 1901, i, 548) as *m*-nitrobenzenyloxime, but is more probably 3 : 4-di-*m*-nitrophenylfurazan; (4) di-*m*-nitrobenzildioxime. *m*-Nitrobenzaldoxime peroxide is also obtainable in small proportion by oxidising the oxime with either potassium ferricyanide or sodium hypochlorite.

When heated at 50° in suspension in benzene, the peroxide yields di-*m*-nitrobenzaldoxime peroxide, 3 : 4-di-*m*-nitrophenylfurazan, *m*-nitrobenzoic acid in large proportion, and a small proportion of a compound which crystallises in colourless, rhombic plates, m. p. 124°, but has not yet been identified. T. H. P.

**Dehydration of Phenylhydrobenzoin.** STEFAN DANILOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 282—289).—The dehydration with 10% sulphuric acid of phenylhydrobenzoin results in a mixture of

triphenylvinyl alcohol and triphenylacetaldehyde, in the proportions 4:1. Garder (*Bull. Acad. roy. Belg.*, [iii], 34, 94), who used phosphoric oxide for the dehydration, obtained the same products, but erroneously identified the second of them as triphenylethylene oxide. Triphenylacetaldehyde has been described by Schmidlin (A., 1910, i, 368) as a substance of m. p. 218°, but it appears that he was mistaken in considering the substance he obtained as triphenylacetaldehyde, and the compound now obtained melts at 105–106°. Oxidation with chromic anhydride converted it into a mixture of triphenylacetic acid and triphenylcarbinol, whilst alcoholic potash gave triphenylmethane. *Triphenylacetaldoxime*, colourless rhombic prisms, m. p. 190°, and the *semi-carbazone*, m. p. 223°, and *phenylhydrazone*, m. p. 142°, of triphenylacetaldehyde were prepared. By the reduction with sodium amalgam of the phenylhydrazone, triphenylethylamine, m. p. 130–131°, was obtained. Aluminium amalgam converts the aldehyde into *triphenylethanol*, m. p. 110–111°, the *phenylurethane* of which m. p. 205–206°, was prepared. Phosphoric oxide acts on the aldehyde to give triphenylvinyl alcohol, showing that a tendency exists for the aldehyde to isomerise to a ketonic form. R. T.

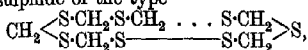
#### The Behaviour of certain Aromatic Hydroxyaldehydes.

A. WINDAUS and H. SCHIELE (*Ber.*, 1923, 56, [B], 846–848).—Benzaldehyde is converted by iodine and dilute potassium hydroxide solution at the atmospheric temperature into benzoic acid in good yield. Under similar conditions, salicylaldehyde loses the aldehydic group as formic acid and yields iodophenol; it is preferable to use an excess of iodine which causes the almost exclusive production of 2:4:6-tri-iodophenol, whereas a mixture of iodophenols is otherwise produced. The behaviour of *p*-hydroxybenzaldehyde is similar. *m*-Hydroxybenzaldehyde, on the other hand, gives an *iodo-m-hydroxybenzoic acid*, needles, m. p. 219–220° (*methyl ester*, colourless needles, m. p. 49°), in which the position of the iodine atom has not been established. 6-Hydroxy-*m*-tolualdehyde and  $\beta$ -naphthol-1-aldehyde behave similarly to *o*- and *p*-hydroxybenzaldehydes, the former giving 3:5-di-iodo-4-hydroxytoluene, m. p. 61–61.5°, and the latter yielding  $\alpha$ -iodo- $\beta$ -naphthol, m. p. 92.5°.

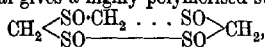
Catalytic hydrogenation of salicylaldehyde dissolved in glacial acetic acid at the atmospheric temperature and pressure in the presence of spongy platinum gives *o*-cresol; under similar conditions,  $\beta$ -naphthol-1-aldehyde is converted into  $\alpha$ -methyl- $\beta$ -naphthol. H. W.

**Isomerism of Thioaldehydes.** EMIL FROMM and CARLTHE SCHULTIS (*Ber.*, 1923, 56, [B], 937–947).—Baumann and Fromm have shown in a series of communications that thioaldehydes occur usually in trimeric, but also in other polymeric forms, and that under the most varied conditions it is possible to obtain only single trithioformaldehyde or trithioacetone, whereas many other aldehydes give two isomeric trithioaldehydes. The substances have been regarded as cyclic sulphides, and their occurrence in different modifications has been explained in accordance with the principle

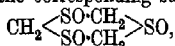
*cis-trans*-isomerism. This conception appeared adequate until Hinsberg (A., 1912, i, 546; 1913, i, 818; 1914, i, 185, 797) announced discovery of a second  $\beta$ -trimethylene trisulphide, and of a third trithiobenzaldehyde, the existence of which is not explicable on the theory of stereoisomerism. A repetition of Hinsberg's work has shown that the compounds described by him do not exist. The crude product obtained by the action of hydrogen sulphide on formaldehyde in the presence of hydrochloric acid has the same melting point ( $216^\circ$ ) as pure trimethylene trisulphide. The compounds, however, are not identical. The crude material is a highly polymerised disulphide of the type



which loses a small amount of sulphur when recrystallised and yields pure trimethylene trisulphide, m. p.  $216^\circ$ , in accordance with the scheme:  $(\text{H}_2\text{CS})_2 + \text{S} \rightarrow x/3(\text{H}_2\text{CS})_3 + \text{S}$ . It is converted by concentrated hydriodic acid into the highly polymerised di-mercaptan,  $\text{HS-CH}_2\text{-S-CH}_2\text{-S} \dots \text{CH}_2\text{-S-CH}_2\text{-SH}$ , decomp.  $247^\circ$ , which loses small amounts of hydrogen sulphide when recrystallised and gives trimethylene trisulphide, m. p.  $216^\circ$ . The latter cannot be transformed by any known method into the mercaptan or disulphide. The products also behave differently when oxidised. The crude material gives a highly polymerised sulphoxide,



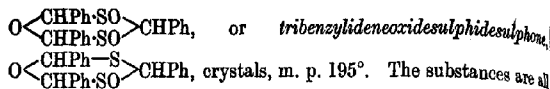
which is reduced to the mercaptan, decomp.  $247^\circ$ , whereas the trimethylene trisulphide yields the corresponding sulphoxide,



comp.  $270^\circ$ , which, when reduced with hydriodic acid, gives trimethylene trisulphide, m. p.  $216^\circ$ , and its *di-iodide*,  $\text{C}_3\text{H}_6\text{S}_3\text{I}_2$ , small, dark red leaflets, m. p.  $100-110^\circ$ , and *tetraiodide*,  $\text{C}_3\text{H}_6\text{S}_3\text{I}_4$ , dark violet prisms, decomp.  $100-105^\circ$ , but not the substance, comp.  $247^\circ$ .

With tribenzylidene trisulphides the relationships are more complicated but Hinsberg's main error appears to consist in the supposition that the pure  $\alpha$ - and  $\beta$ -varieties yield different oxidation products when treated with hydrogen peroxide. This is, however, possible since in the presence of even a deficiency of the reagent the  $\alpha$ -form is converted into the  $\beta$ -modification and the oxidation products are therefore necessarily derived from the latter. The products obtained by treating tribenzylidene trisulphide with small amounts of hydrogen peroxide are *tribenzylidene trisulphide*,  $\text{SO} \begin{array}{c} \text{CHPh} \\ \text{CHPh} \end{array} \text{SO} > \text{CHPh}$ , small needles, m. p.  $240^\circ$ , *tribenzyl-*

*idene trisulphone*,  $\text{SO}_2 \begin{array}{c} \text{CHPh} \\ \text{CHPh} \end{array} \text{SO}_2 > \text{CHPh}$ , a white, chalky powder which does not melt below  $340^\circ$  (the sodium salt,  $\text{C}_{21}\text{H}_{17}\text{O}_6\text{S}_3\text{Na}$ , potassium salt,  $\text{C}_{21}\text{H}_{17}\text{O}_6\text{S}_3\text{K}$ , additive compound with pyridine,  $\text{C}_{21}\text{H}_{18}\text{O}_6\text{S}_3\text{C}_5\text{H}_5\text{N}$ , slender needles, and the *dimethyl* derivative, m. p.  $248^\circ$ , are described), and *tribenzylideneoxocidedisulphoxide*,



The substances are all stable towards aqueous solutions of alkali hydroxides, by means of which they can be separated from one another. Since this treatment also causes the production of benzaldehyde and sulphur dioxide, there are always components of the crude product which are unstable towards alkali, but have not been investigated further. The tetroxide and pentoxide which have been described by Hinsberg are mixtures of these three or four products. Reduction of the trisulphoxide by hydriodic acid gives a product which usually contains iodine and has m. p.  $180-215^{\circ}$  according to the degree of purity. When recrystallised, it yields pure  $\beta$ -tribenzylidene trisulphide, m. p.  $216^{\circ}$ . The product is invariably crude  $\beta$ -trithiobenzaldehyde and not the new  $\delta$ -isomeride, as assumed by Hinsberg.

If  $\alpha$ - or  $\beta$ -tribenzylidene trisulphide is oxidised with a large excess of hot hydrogen peroxide, a product, decomp.  $295^{\circ}$ , is obtained which, in consequence of its insolubility, cannot be recrystallised. It is a mixture which is resolved by treatment with aqueous alkali hydroxide solution into tribenzylidenetrisulphide, tribenzylideneoxidedisulphoxide, benzaldehyde, and sulphur dioxide.

H. W.

**The Oxidation of 1:3-Dimethylcyclohexan-4-one, and the Synthesis of cyclopentane Diketones.** MARCEL GODCHOT (*Compt. rend.*, 1923, 176, 1151-1153).—The oxidation of 1:3-dimethylcyclohexan-4-one with cold 3% aqueous permanganate furnished a 70% yield of  $\delta$ -acetyl- $\gamma$ -methylvaleric acid together with a small amount of  $\beta$ -methyladipic acid formed by the further oxidation of the ketonic acid. The  $\delta$ -acetyl- $\gamma$ -methylvaleric acid is a colourless liquid, b. p.  $177^{\circ}/20$  mm., with  $n_D^{20}$  1.4599, and  $d_4^{20}$  1.078. Its semicarbazone melts at  $136^{\circ}$ , and the ethyl ester boils at  $130^{\circ}/18$  mm., and has  $d_4^{17}$  0.9715, and  $n_D^{17}$  1.4334. The internal condensation of this ester by means of sodium ethoxide gave a 75% yield of a  $\beta$ -diketone, 2-acetyl-1-methylcyclopentan-3-one,  $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \\ \text{CH}_2-\text{CHMe} \end{array} > \text{CH}:\text{COMe}$ , an agreeably smelling liquid, b. p.  $89-90^{\circ}/12$  mm., and having  $d_4^{16}$  1.029, and  $n_D^{16}$  1.4756. It gives an intense violet coloration with ferric chloride, and forms with semicarbazide a disemicarbazone,  $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_4$ , m. p.  $240^{\circ}$  (decomp.), and a carbamylpyrazole, m. p.  $120^{\circ}$ , arising from the anhydriation of the monosemicarbazone. On treatment with sodium and methyl iodide, the  $\beta$ -diketone was converted into 2-acetyl-1:2-dimethylcyclopentan-3-one, a colourless liquid, b. p.  $99-100^{\circ}/14$  mm., and having  $d_4^{17}$  1.020, and  $n_D^{17}$  1.4585. Its monosemicarbazone melts at  $240^{\circ}$ . On treatment with aqueous alkali hydroxide, it is converted into  $\delta$ -acetyl- $\gamma$ -methylhexoic acid, b. p.  $164^{\circ}/10$  mm., with  $d_4^{15}$  1.055, and  $n_D^{15}$  1.4631; the ethyl ester has b. p.  $134-135^{\circ}/13$  mm.,  $d_4^{13}$  0.9865, and  $n_D^{13}$  1.4488.

G. F. M.

**Action of Ammonium Cyanide on Diketones.** H. D. DAKIN and C. R. HARRINGTON (*J. Biol. Chem.*, 1923, 55, 487—494).—A study of the action of ammonium cyanide on  $\alpha$ -diketones, with a view to the synthesis of homologues of diaminosuccinic acid, has shown that the reaction does not result, as expected, in the formation of aminonitriles, but usually leads to a fission of the carbon chain between the two carbonyl groups. Thus, benzil is converted practically quantitatively into benzamide and benzaldehyde cyanohydrin, the same products being also formed by the action of ammonia on benzil dicyanohydrin; anisil, piperil, and furil undergo analogous decompositions; *m*-dinitrobenzil yields *m*-nitrobenzamide and an oil which is probably a condensation product between *m*-nitrobenzaldehyde or its cyanohydrin and dinitrobenzil, and is converted into a glyoxaline derivative when heated with sodium hydroxide and acidified; diacetyl and phenylglyoxal appear to give glyoxaline derivatives. The following ketones are practically unaffected by ammonium cyanide: benzoin, distyryl ketone, benzoylacetone. E. S.

**The Electrolytic Oxidation of Benzene to *p*-Benzoquinone, and the Electrolytic Reduction of Quinone.** A. SEYEWETZ and G. MIRON (*Bull. Soc. chim.*, 1923, [iv], 33, 449—459).—A study was made of the conditions governing the electrolytic oxidation of benzene with the object of securing a maximum yield of *p*-benzoquinone. The optimum conditions whereby a yield of 65% of *p*-benzoquinone was obtained were found to lie within very narrow limits, and are summarised as follows: Electrodes of pure lead with a very homogeneous surface, separated by a diaphragm of porous pot unattackable by sulphuric acid. A current density of 4 amperes per sq. decm., under 3.2—3.5 volts. An electrolyte consisting of a solution containing 25% of sulphuric acid, 33% of acetic acid, with which is emulsified two-thirds of its volume of benzene in presence of 1.0—1.5% of finely divided lead sulphate as catalyst. The temperature must be maintained at 24°, and as soon as the benzene contains 1% of benzoquinone in solution it must be transferred from the anodic compartment to the cathode, otherwise a destruction of the *p*-benzoquinone commences, which rapidly diminishes the yield. The emulsion is produced by means of a helicoid stirrer rotating at 1,200 revolutions per minute inside the anodic compartment. The yield of *p*-benzoquinone rapidly falls with rise in temperature, and becomes zero at 55°. Traces of silica dissolved in the electrolyte cause a notable decrease in the yield. The reduction of the *p*-benzoquinone to quinol when the benzene solution is transferred to the cathodic compartment is practically quantitative. The optimum temperature is 40°, and the presence of 1% of vanadic acid as catalyst is advantageous. The quinol is dissolved by the aqueous electrolyte as it is formed, and the concentration can be allowed to increase to the saturation point without any disadvantage. The benzene, thus freed from *p*-benzoquinone is then returned to the oxidising cell and the process is thus rendered continuous. G. F. M.

**Synthesis of 4-Hydroxy-1 : 2-dimethylantraquinone.**  
 ARTHUR FAIRBOURNE and JOHN MILDRED GAUNTLETT (T., 1923,  
 123, 1137—1139).

**A New Class of Free Organic Radicles. II.** ROLAND SCHOLL [with HERBERT HÄHLE] (*Ber.*, 1923, 56, [B], 918—936; cf. A., 1921, i, 872).—Further investigation of the benzoyloxanthronyls has led the authors to a somewhat modified conception of their constitution. They are now regarded as members of a class of nitrogen-free organic radicles which were hitherto without analogues. They are distinguished from the triarylmethyls and the metallic ketyls by their slight sensitiveness to free oxygen and, in particular, by their ability to react with three atoms of bromine or to acquire three hydroxyl groups when titrated with permanganate until colourless. They appear to behave as trivalent radicles, but this is only apparent, since only two of the three equivalents of bromine or hydroxyl are retained, whereas the third removes the hydroketyl hydrogen in the second phase of the reaction in the form of hydrogen bromide or water, so that ultimately only one valency is saturated. In reality, therefore, they are univalent radicles. This is directly shown by the reaction with permonosulphuric acid, whereby only one hydroxyl group is introduced. Incidentally, this group also indirectly removes the hydroketyl hydrogen as water, so that ultimately in the final product one valency less is saturated than in chlorobenzoyloxanthronyl. Both processes, however, are characteristic of a univalent radicle. Towards chromic acid, the oxanthronyls appear to behave as bivalent radicles, probably as a consequence of the formation of peroxides.

The benzoyloxanthronyls are, however, univalent radicles of a peculiar type, and contain the characteristic arrangement of atoms indicated in the annexed formula. The hydrogen atom closes an internally-complex, seven-membered ring and shares its affinity with the two carbonyl oxygen atoms, so that these make demands on the two radicle-carbon atoms intermediate between those of carbonyl oxygen atoms and ordinary hydroxy-oxygen. The affinity of the free radicle valency is therefore not concentrated on a single trivalent carbon atom as in the triaryl-methyls or the simple metallic ketyls, but is distributed, generally in a non-uniform manner, over two carbon atoms. The benzoyloxanthronyls therefore contain two carbon atoms which may be regarded as together being septavalent. They are distinguished from the "true" carboxylic acids according to the conception of Hantzsch by their radicle nature, and before all by the firmness of retention and non-ionisability of the hydrogen atom.

1-*p*-Chlorobenzoyl-9-oxanthronyl is prepared according to the method of Schaarschmidt (A., 1915, i, 566, 696; 1916, i, 408) by treatment of 1-*p*-chlorobenzoylantraquinone with aluminium bronze and concentrated sulphuric acid, but satisfactory results are only obtained if the pure ketone is used as initial material. Reduction can also be effected with stannous chloride and glacial

acetic acid or by ferrous sulphate in glacial acetic and hydrochloric acids. The molecular weight of the substance in freezing nitrobenzene corresponds with the simple formula,  $C_{21}H_{13}O_3Cl$ . The sulphate,  $C_{21}H_{13}O_3Cl \cdot 2H_2SO_4$  (cf. Schaarschmidt, *loc. cit.*), has now been isolated in the homogeneous condition in the form of dark emerald-green needles. Oxygen does not appear to react with the compound dissolved in nitrobenzene in the dark during four hours at the atmospheric temperature, and attacks it but slowly when the temperature is raised. In daylight, the substance disappears, but only twice as rapidly as when it is illuminated under carbon dioxide. In either case, the reaction is one of dehydrogenation of the *p*-chlorobenzoyloxanthronyl to *p*-chlorobenzoylanthraquinone. Under carbon dioxide, the oxanthronyl itself, and possibly the solvent, act as hydrogen acceptors, whereas in the presence of oxygen this rôle is played by the gas and the primarily formed hydroperoxide, the presence of which cannot be established at any stage of the reaction.

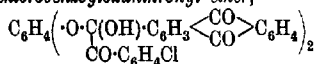
The product of the action of bromine on *p*-chlorobenzoyloxanthronyl has been isolated by cautiously adding the latter to an excess of the halogen. Analyses of the not perfectly homogeneous product indicate the composition  $C_{21}H_{11}O_3ClBr_2$ . The product is transformed into bromine and *p*-chlorobenzoylanthraquinone when heated with water or acetic acid.

*p*-Chlorobenzoyloxanthronyl dissolved in nitrobenzene can be sharply titrated with acid permanganate solution, three equivalents of oxygen being required for the decolorisation of each molecule; the primary product has not been isolated, but chlorobenzoylanthraquinone and iodine are obtained when it is treated with potassium iodide and steam.

Titration of *p*-chlorobenzoyloxanthronyl with chromic acid can be effected when the former is dissolved in nitrobenzene and the latter in glacial acetic acid, or both are dissolved in concentrated sulphuric acid. In either case, one atomic proportion of oxygen is required for each molecule of the ketone.

*p*-Chlorobenzoyloxanthronyl is rapidly converted by nitric acid or nitrogen peroxide into *p*-chlorobenzoylanthraquinone; on the other hand, it appears to be stable in nitrobenzene solution towards nitric oxide.

*Quinolbis-p-chlorobenzoyloxanthronyl ether*,



is prepared as a white powder with a pale yellow tint by the action of *p*-benzoquinone on *p*-chlorobenzoyloxanthronyl in the presence of glacial acetic acid. It is perfectly stable at the atmospheric temperature even in the presence of air. It begins to dissociate at about  $100^\circ$ , and at  $130$ – $140^\circ$  exhibits the dark bluish-violet colour proper to the oxanthronyl, whilst *p*-benzoquinone sublimes. In solution, dissociation commences at the atmospheric temperature so that they show the same colours as very dilute solutions of the radicle itself. The addition of the quinone appears to take place in two stages; the union of molecular proportions of the components

occurs slowly, after which the second molecule of the radicle is rapidly added.

H. W.

**Ethyl Fenchylxanthate.** SERGEI S. NAMETKIN and (MILE) A. S. SELIVANOVA (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 417—425).—Ethyl fenchylxanthate gives on decomposition a mixture of *cyclo*-fenchene and fenchene. Pure fenchyl alcohol is shown to melt at 49°, not at 45°, as is generally accepted, the lower m. p. being due probably to the presence of an isomeric isofenchyl alcohol.

R. T.

**A Method for Resolving some Racemic Alcohols into their Optically Active Components.** A. WINDAUS, F. KLÄNHARDT, and R. WEINHOLD (*Z. physiol. Chem.*, 1923, **126**, 308—312).—The double compound of the alcohol with digitonin is formed (cf. this vol., i, 590), and on recrystallising this compound resolution is obtained, and the alcohol is then obtained free from digitonin by distillation in a vacuum or in steam. In this way, resolution has been effected of *dl*- $\alpha$ -terpineol, *dl*- $\alpha$ -tetrahydro- $\beta$ -naphthol, and of carvomenthol. Phenylmethylcarbinol, on the other hand, remained inactive.

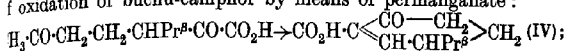
W. O. K.

**Homologues of Camphor.** I. S. S. NAMETKIN and (MILE) ANNA M. CHUCHRIKOVA (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 254—263).—6-Methylcamphor, b. p. 213—213.5°/767 mm., m. p. 168—168.5, is synthesised in the following way. Methylfenchyl alcohol is prepared by the action of magnesium methyl iodide on fenchene, and converted into methylfenchene by dehydration with potassium hydrogen sulphate. Boiling with glacial acetic acid converts methylfenchene into *acetylmethylisoborneol*, b. p. 110°/14 mm.,  $d_4^{20}$  0.9714,  $n_D^{20}$  1.4634, and this, on hydrolysis, gives *methylisoborneol*, m. p. 191—192°, b. p. 219—219.5°/753 mm. Its *phenylurethane*, m. p. 101—102°, and *hydrogen phthalate*, m. p. 167—168°, were prepared. By means of strong nitric acid methylisoborneol is converted into methylcamphor, the *semicarbazone* of which, m. p. 251°, and *oxime*, m. p. 131—132°, were prepared. *Methylborneol*, b. p. 219—220°/758 mm., m. p. 183—184°, was prepared by acting on methylcamphor with sodium in alcoholic solution, and its *phenylurethane*, white needles, m. p. 108°, and *hydrogen phthalate*, m. p. 186°, were prepared. Oxidation of methylcamphor with alkaline potassium permanganate gives *methylciscamphoric acid*, m. p. 185—186°, which on heating is changed into the *anhydride*, m. p. 205—206°.

R. T.

**Catalytic Oxidations with Platinum Black.** I. Oxidation of *Buchu-camphor*. GUIDO CUSMANO (*Gazzetta*, 1923, **53**, i, 153—164).—When exposed in ethereal solution to the action of oxygen or air in presence of platinum black, *buchu-camphor* is rapidly converted principally into four compounds, forming two pairs of related compounds: (a)  $C_{10}H_{18}O_4$  (I) and  $C_{10}H_{16}O_4$  (II); these compounds, previously unknown, retain the *cymene* skeleton, and the first of them is readily converted into the second, which exhibits the phenolic behaviour of *buchu-camphor* and is named

provisionally oxybuchu-camphor. (b)  $C_{10}H_{18}O_4$  (III) and  $C_{10}H_{14}O_3$  (IV). Compound (IV) is an acid and was described by Semmler and Mackenzie (A., 1906, i, 373), who obtained it by the internal dehydration of an open-chain acid occurring among the products of oxidation of buchu-camphor by means of permanganate:



this open-chain acid may possibly represent an intermediate stage in the formation of compound (IV) by the action of lead peroxide, in the presence of dilute sulphuric acid, on compound (III), to which is ascribed the formula  $OH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CHPr^s \cdot CO \cdot CO_2H$ . This action of lead peroxide results also, at the same time, in elimination from acid (III) of carbon dioxide, with formation of another acid, which may have either the formula  $OH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CHPr^s \cdot CO_2H$ , or a lactonic or ketonic structure. In addition to the above four products, the oxidation of buchu-camphor by oxygen in presence of platinum black yields small proportions of an oxythymoquinone and of another compound, not yet characterised.

The compound  $C_{10}H_{18}O_4$  (I) crystallises in colourless, irregularly hexagonal laminae of vitreous lustre, m. p.  $126^\circ$  (decomp.).

*Oxybuchu-camphor*,  $C_{10}H_{16}O_3$ , formed from the preceding compound either by heating it at its melting point or by decomposing potassium salt by means of carbon dioxide, crystallises in colourless, transparent rhombs, m. p.  $75-76^\circ$ , has a faint, pleasant odour resembling that of thymol, volatilises unchanged, and in alcoholic solution gives a violet-black coloration with ferric chloride.

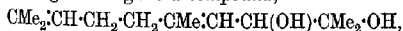
The acid,  $C_{10}H_{18}O_4$  (III, see above), forms long, colourless, prisms, acicular crystals containing water of crystallisation, which is lost in a desiccator. It is monobasic and forms crystalline ammonium and barium salts and a sparingly soluble silver salt.

For compound (IV), even when prepared as described by Semmler and Mackenzie (*loc. cit.*), the m. p.  $190^\circ$  is found, these authors giving p.  $182^\circ$ . T. H. P.

**Chemical Actions of Light.** G. SCAGLIARINI and GIUSEPPINA ADAMI (*Gazzetta*, 1923, 53, i, 135-139).—The indirect auto-oxidations of certain compounds have been investigated.

Fenchone and toluene, exposed for some months to the action of light in presence of oxygen and water, yielded carbon dioxide, benzoic and acetic acids. Under similar conditions, fenchone in alcohol gave carbon dioxide, acetic acid, a small proportion of oxalic acid, and a compound, b. p.  $83^\circ$ , containing 49.39% C and 11.32% H. Pinene and oxalic acid yielded a large proportion of resin, together with acetic acid.

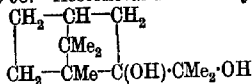
Acetone and geraniol gave a compound,



a liquid, b. p.  $208-210^\circ/14$  mm.,  $d_4^{20} 0.96$ . Acetone and menthol

gave the compound  $\begin{smallmatrix} CHMe \cdot CH_2 \cdot C(OH) \cdot CMe_2 \cdot OH \\ CH_2 \cdot CH_2 - CH \cdot CHMe_2 \end{smallmatrix}$ , b. p.  $197-$

200°/15 mm.,  $d$  0.95. Acetone and borneol yielded the compound



b. p. 160°/20 mm.,  $d$  0.99.

T. H. P.

**The Action of Hypochlorous Acid on Bornylene.** GEORGE GERALD HENDERSON and JOHN ALEXANDER MAIR (T., 1923, 1155—1161).

**Pinocamphane.** S. S. NAMETKIN and ANNA JARZEV (Ber 1923, 56, [B], 832—833).—Pinocamphone is converted by hydrazine hydrate at 190—200° into the corresponding *hydrazone*, colourless liquid of unpleasant odour, b. p. 134—135°/22 mm  $d_{20}^{20}$  0.9917,  $n_D^{20}$  1.5155, which is transformed by potassium hydroxide in the presence of platinum on fused clay or by sodium ethoxide, at 170—180° into *pinocamphane* (annexed formula), b. p. 163.5—164°/747 mm., 164.5—165°/763 mm  $d_{20}^{20}$  0.8558,  $n_D^{20}$  1.4611. The product does not appear to be identical with the dihydropinene obtained previously by the authors by the catalytic hydrogenation of *l*- $\alpha$ -pinene by Sabatier's method.

H. W.

**West Australian "Sandalwood Oil."** B. SANJIVA RAO and J. J. SUDBOROUGH (J. Ind. Inst. Sci., 1923, 5, 163—176).—The so-called West Australian sandalwood oil is derived from a tree (*Fusanus spicatus*, R.Br.) quite different from *Santalum alba* Linn., from which genuine East Indian sandalwood oil is obtained. It has  $d$  15/15°, 0.957—0.972;  $n_D^{25}$  1.5019—1.510;  $[\alpha]_D^{25}$  -0.2° to -7.7°; total alcohols as santalol ( $\text{C}_{15}\text{H}_{24}\text{O}$ ), 69.3—80.0%; esters as santalyl acetate, 2.3—6.5%; acid value, 2.4—5. The alcohols present are isomeric with the two santalols present in East Indian oil and have been termed  $\alpha$ - and  $\beta$ -fusanols. The fusanols yield hydrogen phthalates and phenylurethanes. The fact that they react much more slowly than the santalols with phthalic anhydride indicates that they are probably secondary, not primary alcohols. From their molecular refractions it is probable that the fusanols are bicyclic compounds containing two olefine linkages.  $\alpha$ -Fusanol,  $\text{C}_{15}\text{H}_{24}\text{O}$ , has b. p. 146—149°/5 mm.,  $d_{15}^{15}$  0.9775,  $n_D^{25}$  1.50,  $[\alpha]_D^{25}$  +5.7°.  $\beta$ -Fusanol has b. p. 153—155°/5 mm.,  $d_{15}^{15}$  0.97,  $n_D^{25}$  1.5100,  $[\alpha]_D^{25}$  +26°.

H. C. R.

**$\beta$ -Amyrin from Manilla Elemi Resin.** II. ALEXANDER ROLLETT and KLOTHILDE BRATKE (Monatsh., 1923, 43, 685—686, cf. this vol., i, 476).—Potassium persulphate converts  $\beta$ -amyrin in acetic acid solution, in presence of sulphuric acid, into  $\beta$ -amyrin acetate, leaflets, m. p. 291—292°, soluble in concentrated sulphuric acid to give a yellow solution with a reddish-violet fluorescence. The acetate, on hydrolysis with methyl-alcoholic sodium hydroxide, gives *oxy*- $\beta$ -amyrin,  $\text{C}_{30}\text{H}_{47}\text{O}\cdot\text{OH}$ , prisms, m. p. 20



$\alpha$ - and  $\beta$ -forms which are presumably more stable than the corresponding forms of glucose. Sinigrin has been obtained in an anhydrous form,  $C_{10}H_{16}O_9NS_2K$ , compact, white, glistening needles, m. p.  $79^\circ$ ,  $[\alpha]_D -16.13^\circ$  (in water). This indicates that the decomposition of sinigrin by the enzyme myrosin is a simple hydrolysis,  $C_{10}H_{16}O_9NS_2K + H_2O = C_3H_5 \cdot NCS + C_6H_{12}O_6 + KHSO_4$ . W. O. K.

**Some Additive Compounds of Digitonin.** A. WINDAUS and R. WEINHOLD (*Z. physiol. Chem.*, 1923, 126, 299—307).—The following additive compounds of digitonin with alcohols and phenols are described.  *$\alpha$ -Naphtholdigitonin*,

$C_{55}H_{90}O_{29} \cdot C_{10}H_8O \cdot 8H_2O$ , very fine needles.  *$\beta$ -Naphtholdigitonin*,  $C_{55}H_{90}O_{29} \cdot C_{10}H_8O \cdot 10H_2O$ . *p-Bromophenoldigitonin*,  $C_{55}H_{90}O_{29} \cdot C_6H_5OBr \cdot 8H_2O$ , fine needles. *Phenyl mercaptan-digitonin*,  $C_{55}H_{90}O_{29} \cdot C_6H_5S \cdot 6H_2O$ . *Carvomentholdigitonin*,  $C_{55}H_{90}O_{29} \cdot C_{10}H_{20}O \cdot 10H_2O$ , fine needles. *1- $\alpha$ -Terpinolol-digitonin*,  $C_{55}H_{90}O_{29} \cdot C_{10}H_{18}O \cdot 6H_2O$ , very fine needles. *d- $\alpha$ -Terpineol-digitonin*,  $C_{55}H_{90}O_{29} \cdot C_{10}H_{18}O \cdot 8H_2O$ . *ac-Tetrahydro- $\beta$ -naphthol-digitonin*,  $C_{55}H_{90}O_{29} \cdot C_{10}H_{12}O \cdot 8H_2O$ , fine needles. *Phenylmethylcarbinol-digitonin*. *sec-Octylalcohol-digitonin*. These compounds are decomposed, by distillation either in a vacuum, or in steam.

W. O. K.

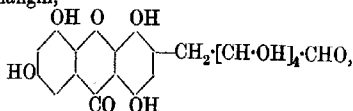
**Betulin.** K. ALB. VESTERBERG (*Ber.*, 1923, 56, [B], 845; cf. Vesterberg, A., 1922, i, 825; Schulze and Pieroh, A., 1922, i, 1045; Dischendorfer, this vol., i, 123).—Elementary analysis and, in particular, determination of the saponification number of crystalline betulin diacetate, m. p.  $218-218.5^\circ$ , lead the author to regard the presence of 30 carbon atoms in the betulin molecule as definitely established. In the formula,  $C_{30}H_{48}(OH)_2$ , which has also been proposed by Dischendorfer, the uncertainty with regard to the number of hydrogen atoms does not exceed two. H. W.

**Betulin. III.** IVAN KONSTANTINOVITSCH TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 381—394; cf. A., 1912, i, 260, 972).—*Betulin dibutyrate*,  $C_{34}H_{58}O_8(C_4H_7O)_2$ , m. p.  $107^\circ$ , has been prepared, thus establishing the hydroxylic nature of the two oxygen atoms of betulin. Betulin, on oxidation with potassium permanganate in acetic acid solution, gives *oxybetulin*,  $C_{28}H_{46}O_3$ , m. p.  $205-206^\circ$ , which yields an *acetate*, m. p.  $181-182^\circ$ ; the latter derivative being also obtained by the oxidation of betulin diacetate. Oxybetulin, on oxidation, gives *dehydrodioxybetulin*,  $C_{28}H_{38}O_4$ , m. p.  $256^\circ$ , which on further oxidation gives a substance not melting below  $310^\circ$ , and containing inorganic matter. As final products of oxidation were obtained *betulinic acid*,  $C_{14}H_{22}O_3$ , m. p.  $277^\circ$ , and a *lactone*,  $C_{15}H_{22}O_3$ , m. p.  $303^\circ$ . Betulinamic acid,  $C_{28}H_{38}O_{10}N_2$ , is shown to contain one nitro- and one nitrile group. From the above and preceding articles, it is concluded that betulin is a substance of the sterol type, and contains one primary and one secondary hydroxyl group, four saturated rings, and one double linking, situated on the chain joining the rings. One of the hydroxyl groups must be in the  $\beta$ - or  $\gamma$ -position to this double linking.

R. T.

**The Parent Substance of Indian Yellow.** WILHELM WIEHORSKI (*Arch. exp. Path. Pharm.*, 1923, 97, 462—488).—If mangin, which has been extracted from mango leaves, is fed to rabbits, euxanthic acid (Indian yellow) is excreted in the urine. It thus appears that mangin is the parent substance of Indian yellow.

*Mangin*,  $C_{19}H_{18}O_{11}$ , m. p.  $273^{\circ}$ ,  $[\alpha]_D -46^{\circ}$  in alcohol, is only slightly soluble in the usual neutral organic solvents. It crystallises from alcoholic solution in needles, from water in prisms. It is not hydrolysed by emulsin, invertase, or other ferments, and it forms an *octa-acetyl* derivative, an *octabenzoyl* derivative, and a lead salt,  $C_{19}H_{14}O_{11}Pb_2$ . When heated for a long time with hydrochloric acid, it yields lævulinic acid and tetrahydroxyxanthone, which was isolated as the lead salt. The following formula is assigned to mangin,



the position of the hydroxy-groups being uncertain.

Euxanthic acid,  $C_{19}H_{18}O_{11}$ , has the following constants: m. p.  $156\text{--}158^{\circ}$  (decomp.),  $[\alpha]_D -79\cdot43^{\circ}$ ,  $-81\cdot45^{\circ}$  in alcohol.

W. O. K.

**Preparation of Melanin from Benzene.** OSCAR ADLER (*Biochem. Z.*, 1923, 137, 201—205).—By treatment of benzene with successive portions of 3% hydrogen peroxide in presence of 1% aqueous ferric chloride solution, a 2.7% yield of *benzenemelanin* acid is formed, soluble in dilute alkalis and alcohols. When heated at  $270^{\circ}$  it is converted into *benzenemelanin*, a black, amorphous powder insoluble in alkalis or organic solvents.

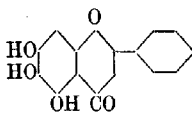
H. K.

**Synthesis of Dicyanine-A.** S. PALKIN (*Ind. Eng. Chem.*, 1923, 15, 379—381).—The conditions affecting the synthesis of dicyanine-A from 6-ethoxy-2:4-dimethylquinoline ethiodide were studied and variations tried in the kind of solvent used, concentration of hydroxyl-ion, type of alkali, catalysts, water, oxygen, time, and temperature. No solvent was found superior to ethyl alcohol, but excellent results were obtained with sodium sulphide; the alkali salt in 95% alcohol. Chloroform acts as a catalyst in the presence of sodium ethoxide, the yield of dye obtained being about twelve times that obtained by Mikeska, Haller, and Adams. The optimum conditions were, 1.5 c.c. of chloroform per 1 g. of intermediate, 25 g. of sodium sulphide ( $Na_2S_9H_2O$ ) in 100 c.c. of 95% alcohol, 1 g. of intermediate to 25 c.c. of alcohol and a temperature of  $50^{\circ}$  for thirty minutes. The dye produced was studied by the Bureau of Standards and found to be an efficient sensitiser.

H. C. R.

**Baicalin, a New Flavone-Glycuronic Acid Compound from the Roots of *Scutellaria baicalensis*.** KEITA SHIBATA, SHÔJIRO YATA, and MAKOTO NAKAMURA (*Acta Phytochim.*, 1923, 1, 105—109).—The name scutellarin was applied by Takahashi to a crystalline compound from *Scutellaria baicalensis*, to which he ascribed

the formula  $C_{10}H_8O_3$  (A., 1890, 64). The same name has, however, been accepted for a flavone-glycuronic acid compound found by Molisch and Goldschmiedt (A., 1902, i, 48) in other species of *Scutellaria*, and it is proposed to call Takahashi's compound *wogonin* (from "wogon," the Japanese term for the root). A new compound, *baicalin*, closely allied to scutellarin, occurs in the roots of *S. baicalensis*, and can be extracted from the roots by boiling 50% alcohol, the yield being 12.5% of the weight of dry root. It is a bright yellow, crystalline substance,  $C_{21}H_{18}O_{11}$ , m. p. 223°. When hydrolysed with concentrated sulphuric acid, it is decomposed into glycuronic acid and a flavone derivative, *baicalein*,  $C_{15}H_{10}O_5$ , yellow prisms, m. p. 264–265° (decomp.). A great deal of evidence indicates that baicalein is a trihydroxyflavone, an hydroxychrysin with all three hydroxy-groups in the one phenyl ring. By alkaline hydrolysis, baicalin gives acetophenone, and when fused with potassium hydroxide both baicalin and baicalein give benzoic acid. Baicalein appears to be identical with the 5:6:7-trihydroxy-



flavone (annexed formula) prepared synthetically by Bargellini (A., 1919, i, 545). Evidence that condensation with glycuronic acid to form baicalin takes place at the 6-hydroxy-group is furnished by the observation that baicalin is not oxidised by chloropentamminecobaltchloride, which gives a strong colour reaction with *o*-dihydroxy-compounds but not with corresponding meta-compounds. Scutellarin likewise fails to give a reaction with this reagent, and must therefore be constituted similarly to baicalin.

*Pentabenzoylscutellarin* forms a white, microcrystalline powder, m. p. 237–238° (decomp.).

Baicalin gives with ferric chloride in alcoholic solution a dark green colour, and with lead acetate an orange-red precipitate. It dissolves in alkalis with a yellow colour, and reduces ammoniacal silver nitrate in the cold. It is difficult to alkylate, but forms with diazomethane in acetone solution a *monomethyl* derivative, m. p. 211–212° (decomp.); this contains a free carboxy-group. *Dibromobaicalin* softens above 270°. Baicalin is levorotatory,  $[\alpha]_D^{25} -144.9^\circ$ . *Tetracetylbaicalin* forms microscopic prisms containing  $1H_2O$ , m. p. 256–257°. The fact that only a tetra-acetyl derivative is formed indicates that the glycuronic acid is in the lactone form. A small quantity of what appeared to be a *penta-acetylbaicalin*, m. p. 212–213° (decomp.), was also obtained. *Tetrabenzoylbaicalin* forms a grey, microcrystalline powder, m. p. 229–230°.

*Tribenzoylbaicalein* forms small prisms, m. p. 199.5°. Triacetylbaicalein agrees in properties with Bargellini's triacetyl derivative of 5:6:7-trihydroxyflavone (*loc. cit.*). Free baicalein is present with baicalin in the roots of the plant.

Further investigation of wogonin shows that the substance as analysed by Takahashi contained water of crystallisation. The correct formula is  $C_{18}H_{12}O_4$ , and it contains a methoxy-group. *Acetylwogonin*,  $C_{18}H_{14}O_6$ , forms long, white needles, m. p. 152–

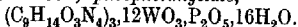
53°; *benzoylwogonin* forms yellowish-white needles, m. p. 170°; *methylylwogonin*,  $C_{16}H_{11}O_3 \cdot OMe, H_2O$ , forms yellowish-white needles, m. p. 180—181°.

Baicalein and scutellarein, like other hydroxyflavones (cf. this vol., ii, 360) show two absorption bands in the ultra-violet, the bands showing shifts such as would be expected from the constitutions of the compounds. In baicalin, the first band disappears, only a broad band at 3500 remaining, but in scutellarin both bands persist, perhaps through the influence of the 4'-hydroxy-group. Wogonin has an unusual spectrum with only one band, at 3500, but acetylwogonin, like triacetylbaicalein, shows the true flavone spectrum.

The green parts of *S. baicalensis* are found to contain scutellarin. The relation between the scutellarin of the leaves and the baicalin of the roots is a question of great biochemical interest.

E. H. R.

**The Extractive Substances of Muscle. Carnosine and its derivatives.** IVAN A. SMORODINCEV (*J. Russ. Physiol.*, 1919, 2, 98).—The author reviews the literature of the subject and describes the following new salts of the dipeptide: *Sulphate*, m. p. 238—40°; *orthophosphate*, m. p. 205—207°; *metaphosphate*, m. p. 200—203°; *iodate*, m. p. 188—190°; *oxalate*, m. p. 216—218°; *nitrate*, m. p. 195—200°; *phosphotungstate*,



The *phenylcarbamido*-derivative, m. p. 178—180°, has also been prepared. Carnosine is hydrolysed by erepsin.

E. S.

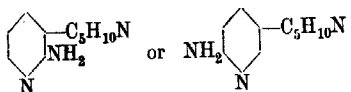
**The Alkaloids of *Corydalis cava*.** ERNST SPÄTH, ERICH LOSETTIG, and OTTMAR TRÖTHANDL (*Ber.*, 1923, 56, [B], 875—79).—During the course of preparation of corydaline from *Corydalis cava*, two new alkaloids, *d*-tetrahydropalmatine and *d*-corypalmine, have been isolated; in the latter, one of the four methoxy-groups of tetrahydropalmatine is replaced by hydroxyl.

The alkaloids from *Corydalis cava* are dissolved in ether and agitated with sodium hydroxide solution to remove phenolic substances. The fully alkylated compounds are dissolved in hydrochloric acid and, from this solution, *d*-tetrahydropalmatine hydrochloride separates in the course of a few days. *d*-Tetrahydropalmatine,  $C_{21}H_{25}O_4N$ , forms colourless crystals which exhibit distinct triboluminescence when crushed. It has m. p. 142°,  $d^{20}_D + 292.5^\circ$  in alcoholic solution. The constitution of the alkaloid is established by its dehydrogenation with iodine and ethyl alcohol and treatment of the product with magnesium methyl iodide which yields a compound identical with that obtained previously by Späth and Lang (*A.*, 1922, i, 166) from palmatine and magnesium methyl iodide. The conception that the dehydro-compound is palmatine is confirmed by direct comparison of the maternal iodides and of the corresponding tetrahydro-derivatives.

The bulk of the bulbocapnine is removed from the phenolic alkaloids; fractional extraction of the solution of the remainder in chloroform with very dilute hydrochloric acid gives corybulbine

and corypalmine. The former has been considered by Dobbin, Lander, and Paliatsens (T., 1901, 79, 89) as corydaline in which one methoxy-group has suffered demethylation. This conception is confirmed by its conversion into dehydrocorybulbine, methylation of the latter, and reduction to the tetrahydro-compound, which is found to be identical with *r*-corydaline, m. p. 135°. The latter is also obtained by the methylation of corybulbine with diazomethane. *Corypalmine* forms small, colourless crystals, m. p. 236–237°,  $[\alpha]_D^{25} +280^\circ$  when dissolved in chloroform; it gives *d*-tetrahydropalmatine when methylated. H. W.

**2-(or 6-)Aminonicotine.** A. E. TSCHITSCHIBABIN and L. A. BUCHHOLZ (J. Russ. Phys. Chem. Soc., 1920, 50, 548–552).—The action of sodamide on nicotine in the presence of an indifferent solvent such as vaseline or toluene leads to the formation of an amino-derivative in a manner similar to that observed with other derivatives of pyridine (see A., 1915, 1, 590). The new substance



may be the 2- or the 6-amino-compound (annexed formulæ) and is obtained in a yield of about 10%. After crystallisation from

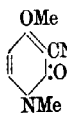
light petroleum it melts at 124–125° and forms biaxial leaflets or plates, probably of the monoclinic system; the *dipicrate* forms long, thin yellow needles, m. p. 223–225°; the *chloroplatinate*, red prisms, contains 2H<sub>2</sub>O, m. p. 244–245°. The action of nitrous acid in the presence of sulphuric acid on aminonicotine leads to 2-(or 6-)*hydroxynicotine*, crystals, m. p. 121–123°; the *dipicrate* forms large, lustrous needles, m. p. 196–198°, and the *chloroplatinate*, small orange crystals, m. p. 246–248°, also occurring in the form of red prisms containing 3H<sub>2</sub>O. G. A. R. K.

**The Morphine Group. I. A Discussion of the Constitutional Problem.** JOHN MASSON GULLAND and ROBERT ROBINSON (T., 1923, 123, 980–998).

**The Morphine Group. II. Thebainone, Thebainol, and Dihydrothebainone.** JOHN MASSON GULLAND and ROBERT ROBINSON (T., 1923, 123, 998–1011).

**Yohimbine (Quebrachine). II. apo-Yohimbine and Deoxy-yohimbine.** GEORGE BARGER and ELLEN FIELD (T. 1923, 123, 1038–1043).

**The Constitution of Ricinine.** ERNST SPÄTH and GROS KOLLER (Ber., 1923, 56, [B], 880–887).—The authors have succeeded in replacing the methoxy-group of ricinine by hydrogen and thereby obtaining a substance which they designate ricinidine. The compound is shown by direct synthesis to be 3-cyano-1-methyl-2-pyridone, so that ricinine must be regarded as 3-cyano-4-methoxy-1-methyl-2-pyridone (annexed formula). The constitution assigned tentatively to ricinine (Späth and Tschelnitz, A., 1922, i, 571) is therefore withdrawn.



Ricinine is converted by potassium hydroxide into ricinic acid (f. Böttcher, A., 1918, i, 304), which is transformed by phosphoryl chloride at  $100^\circ$  into 4-chloro-3-cyano-1-methyl-2-pyridone,  $\text{H}_5\text{ON}_2\text{Cl}$ , m. p.  $159^\circ$ ; the latter is reconverted by a solution of dium in methyl alcohol into a mixture of ricinic acid and ricinine. Hydrogenation of the chloro-compound in the presence of palladised iridium sulphate leads to the production of ricinidine [3-cyano-1-methyl-2-pyridone], b. p.  $243^\circ/18$  mm., m. p.  $140^\circ$ . The latter is hydrolysed successively to the corresponding amide, m. p.  $216^\circ$ , and to the carboxylic acid,  $\text{C}_7\text{H}_7\text{O}_3\text{N}$ , colourless needles, m. p.  $184^\circ$ . The elucidation of the constitution of ricinine depends on the cognition of this acid as 1-methyl-2-pyridone-3-carboxylic acid. For this purpose, the three possible acids, viz. 2-pyridone-1-acetic acid, and 1-methyl-2-pyridone-3- and -6-carboxylic acids, have been synthesised.

2-Pyridone-1-acetic acid,  $\text{CH} \begin{smallmatrix} \text{CH}\cdot\text{CO} \\ \text{CH}\cdot\text{CH} \end{smallmatrix} \text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $220^\circ$ —

$23^\circ$ , is obtained from 2-methoxypyridine and methyl iodoacetate. Methyl-2-pyridone-6-carboxylic acid is prepared with difficulty by the action of methyl iodide on the di-silver salt of 2-hydroxypyridine-6-carboxylic acid; it has m. p.  $247$ — $248^\circ$ . Similar treatment of the di-silver salt of 2-hydroxypyridine-3-carboxylic acid and subsequent hydrolysis of the product leads to the isolation of methyl-2-pyridone-3-carboxylic acid, m. p.  $184^\circ$ , which is identical with the acid obtained from ricinidine; in this instance, also, ethylation is a matter of difficulty, and is more conveniently effected by treating the dry di-sodium salt with methyl iodide. Methyl-2-pyridone-3-carboxylic acid is converted by successive treatment with thionyl chloride and ammonia into the amide, m. p.  $216$ — $217.5^\circ$  [identical with that obtained during the hydrolysis of ricinidine (see above)], which is further transformed by thionyl chloride or phosphoryl chloride into ricinidine.

Further proof of the identity of ricinidine with 3-cyano-1-methylpyridone is deduced from the observation that it is converted by phosphoryl chloride and phosphorus pentachloride at  $150^\circ$  into 4-chloro-3-cyanopyridine, m. p.  $103$ — $105^\circ$ . The synthesis of the latter substance is effected by the successive action of phosphoryl chloride and phosphorus pentachloride and ammonia on 2-hydroxypyridine-3-carboxylic acid whereby 2-hydroxypyridine-3-carboxylide, m. p.  $163$ — $164^\circ$ , is obtained which is transformed by phosphoric oxide into 2-chloro-3-cyanopyridine. H. W.

#### The Nitration of 2-Aminopyridine. A. E. TSCHITSCHIBABIN

and I. G. BYLINKIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 471—474; cf. A., 1922, i, 573).—It has already been shown (cf. A., 1916, 24; 1915, i, 591) that the nitration of 2-aminopyridine leads to the formation of two isomeric nitro-derivatives, the main product being 5-nitro-2-aminopyridine, and the other is now shown to be 3:2-compound. The formation of the latter is favoured by raising the temperature during the isomerisation of the nitroamine from the nitro-compound (cf. above).

When diazotised in the presence of sulphuric acid, the 3:2-compound (m. p. 162°) yields 3-nitro-2-hydroxypyridine, yellow needles, from hot water, m. p. 224°, readily soluble in dilute alkali hydroxides. Diazotisation in hydrochloric acid solution leads to 2-chloro-3-nitropyridine, flattened needles, m. p. 101–102°, insoluble in alkali hydroxides, but feebly basic. All attempts to reduce the 3:2-compound to the corresponding diamine failed.

2-Chloro-5-nitropyridine obtained by the diazotisation of the 5:2-isomeride (cf. A., 1915, i, 591) yields, on reduction with stannous chloride, the corresponding amino-compound identical with that prepared by Mills and Widdows (T., 1908, 93, 1372), m. p. 81–82°. The replacement of the amino-group in this compound by bromine by the Sandmeyer reaction leads to 2-chloro-5-bromopyridine, white plates, m. p. 71°, possessing a strong and characteristic odour. The amino-group in the compound, m. p. 81–82°, like that of 3-aminopyridine, is readily diazotisable, and the diazonium compounds prepared in hydrochloric acid solution couple with  $\alpha$ - and  $\beta$ -naphthol in alkaline solution, giving red substantive cotton dyes which gradually change to brownish-red and orange, respectively; only the latter is fairly stable to acids.

5-Nitro-2-hydroxypyridine (cf. A., 1915, i, 591) is converted through the silver salt into 5-nitro-2-ethoxypyridine, white plates, m. p. 72°. The reduction of this compound with stannous chloride gives a very unstable, oily amine, which is converted by acetic anhydride into 5-acetamido-2-ethoxypyridine, flattened needles, m. p. 122°. G. A. R. K.

**The Bromination of 2-Aminopyridine.** A. E. TSCHITSCHIBABIN and (MLLE) V. S. TIASHELOVA (*J. Russ. Phys. Chem. Soc.* 1920, 50, 483–492).—The nuclear hydrogen atoms of 2-aminopyridine, unlike those of pyridine itself, appear to be readily substituted (cf. A., 1915, i, 591; 1916, i, 224) and bromination proceeds easily, best of all in the presence of one molecular proportion of sulphuric acid. The products are 5-bromo-2-aminopyridine, flattened prisms, m. p. 137° (*picrate*, yellow needles, m. p. 257°), and 3:5-dibromo-2-aminopyridine, white needles, m. p. 105°. The two compounds are separated by means of light petroleum in which the monobromo-compound is sparingly soluble. The dibromo-compound is identical with that described by Fischer and Chur (A., 1916, i, 741) and gives on treatment with nitrous acid the corresponding dibromohydroxy-compound, m. p. 207–208°, previously prepared by Koenigs and Geigy (A., 1884, 1186, 1368).

Diazotisation of the monobromo-compound in the presence of sulphuric acid (cf. preceding abstract) leads to 5-bromo-2-hydroxypyridine, large, sparkling prisms, m. p. 177–178°. Diazotisation in hydrochloric acid solution gives 2-chloro-5-bromopyridine, colourless scales, m. p. 71°, with an odour reminiscent of dibromobenzene volatile in steam, identical with the substance obtained by Tschitschibabin and Bylinkin (preceding abstract). On treatment with sodamide and amyl nitrite (Tschitschibabin and Riasancev, A.

1916, i, 224) an unstable substance is obtained which shows the reactions of an isodiazoxide, giving a red dye with  $\beta$ -naphthol and yielding with hydrochloric acid the chlorobromo-compound mentioned above and with hydrobromic acid 2:5-dibromopyridine, flattened needles, m. p. 94–95°, which sublimes. Nitration of the monobromo-compound dissolved in concentrated sulphuric acid leads to the nitroamine, microscopic needles, m. p. 181° (decomp.), which when heated with sulphuric acid isomerises to 5-bromo-3-nitro-2-aminopyridine, large yellow needles from alcohol, or short needles or prisms from benzene, m. p. 205°.

G. A. R. K.

**The Bromination of Nitro-2-aminopyridines.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 492–494).—It has been shown (preceding abstract) that the bromination of 2-aminopyridine leads to 3- and 5-bromo-compounds. The two nitroaminopyridines should therefore yield two different monobromo-derivatives, one of which should be identical with the nitration product of 5-bromo-2-aminopyridine. This is found to be the case. 5-Nitro-2-aminopyridine, m. p. 188° (cf. A., 1915, i, 591), gives on bromination in the presence of dilute sulphuric acid (20 per cent.) a good yield of 3-bromo-5-nitro-2-aminopyridine, yellow needles, m. p. about 215° (decomp.); the compound is slowly decomposed by light. 3-Nitro-2-aminopyridine, m. p. 162°, gives, when brominated under similar conditions, 5-bromo-3-nitro-2-aminopyridine, m. p. 205°, identical with that obtained by Tschitschibabin and Tiashelova (preceding abstract), thus confirming the constitution previously assigned to the compound melting at 162°.

G. A. R. K.

**The Sulphonation of 2-Aminopyridine.** A. E. TSCHITSCHIBABIN and (MILLE) L. S. TIASHELOVA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 495–497).—Whilst pyridine is sulphonated with considerable difficulty, 2-aminopyridine undergoes sulphonation almost as readily as aniline. When it is heated with fuming sulphuric acid (10%  $\text{SO}_3$ ) at 180° for four to five hours, a sulphonic acid, nodular aggregates of white crystals, m. p. 326–327° (decomp.), is produced. The salts of this acid with metals of the alkali group are very soluble in water, those of calcium, strontium, and barium less so. The sulphonic acid dissolves with difficulty in dilute acids. The orientation of the sulphonic acid is not yet certain, but it is probably the 2:5-aminosulphonic acid. On treatment with nitrous acid, it passes into the corresponding 2-hydroxysulphonic acid which is isolated in the form of its hydrated sodium salt,  $\text{HC}_5\text{H}_3\text{SO}_2\text{Na} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , which loses its water of crystallisation at 25°. Aqueous solutions of the salt give crystalline precipitates with barium and calcium chlorides.

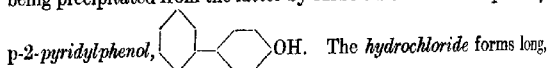
G. A. R. K.

**The Phenylation of 2-Aminopyridine by Ullmann's Method.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 497–502).—2-Aminopyridine readily reacts with bromo- or iodo-benzene in the presence of potassium carbonate and metallic copper, the

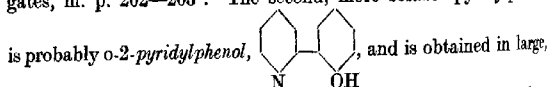
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reaction product being separated into the constituents by distillation at atmospheric pressure. The fraction up to  $240^{\circ}$  contains unchanged starting material, whilst the oil boiling between  $240^{\circ}$  and  $345^{\circ}$  consists mainly of 2-anilinopyridine, m. p.  $108^{\circ}$  (Fischer, A., 1903, i, 52; 1899, i, 635), short, thick prisms; the *picrate* forms prisms, m. p.  $222^{\circ}$ . 2-Diphenylaminopyridine constitutes the highest fraction, b. p.  $345\text{--}370^{\circ}$ , and forms plates, m. p.  $104^{\circ}$ . The *picrate*, prepared in alcoholic solution, melts at  $174^{\circ}$ , and forms plates or long needles; it is more soluble in alcohol and acetone than 2-anilinopyridine *picrate*.  
G. A. R. K.

**The Diazotisation and Diazo-reactions of 2-Aminopyridine.**  
A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 502—511).—Attempts made to introduce the pyridine nucleus into organic compounds by the Grignard reaction on 2-bromo- and 2-iodo-pyridine failed; the preparation of these substances from sodium 2-pyridineisodiazoxide (A., 1916, i, 224) has been improved and is described. Successful results are, however, obtained by the interaction of the latter substance with phenol. After removing phenol, etc., three substances are obtained, one of which may be readily separated owing to its insolubility in alkali hydroxides. This consists of 2-phenoxypyridine, b. p.  $277\text{--}277.5^{\circ}$ , m. p.  $46\text{--}48^{\circ}$ , possessing an odour reminiscent of diphenyl ether, the orange *chloroplatinate*, small prisms, m. p.  $175\text{--}177^{\circ}$ , and the *picrate* were also prepared. The two compounds soluble in alkali are isomeric pyridylphenols, and may be separated by crystallisation from benzene. The less soluble compound separates in white leaflets or thick, lustrous, hexagonal plates containing a molecule of benzene of crystallisation; after removing the latter it melts at  $159\text{--}160^{\circ}$  and is readily soluble both in dilute acids and alkalis, being precipitated from the latter by carbon dioxide. It is probably



slender needles, m. p.  $215\text{--}218^{\circ}$ ; the *chloroplatinate*, large, orange-yellow, flattened needles, m. p.  $210\text{--}211.5^{\circ}$  (decomp.), whilst the sparingly soluble *picrate* is obtained in nodular, crystalline aggregates, m. p.  $202\text{--}203^{\circ}$ . The second, more soluble pyridylphenol



greenish-yellow prisms, m. p.  $56^{\circ}$ ; it is less soluble in alcohol than the preceding compound and its phenolic properties are less marked; the yellow colour may perhaps be due to a quinonoid structure. The *hydrochloride* is obtained in a hydrated form, colourless prisms, m. p.  $56^{\circ}$ , which lose water in a desiccator, the anhydrous substance melting at  $167\text{--}170^{\circ}$ . The *chloroplatinate*, microscopic needles, softens at  $227\text{--}228^{\circ}$ . The *picrate* forms slender, long, yellow needles, m. p.  $174^{\circ}$ .  
G. A. R. K.

**Di-2-pyridylamine.** A. E. TSCHITSCHIBABIN and M. A. VOROBYEV (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 519—522).—Di-2-pyridylamine was originally obtained by Tschitschibabin and Zeide (A., 1915, i, 590), and also by Steinhäuser and Diepolder (A., 1916, **739**), by heating 2-chloropyridine with 2-aminopyridine in the presence of zinc chloride or barium oxide. It is now shown that the best method of preparing this substance consists in heating 2-aminopyridine with its hydrochloride; a yield of 40% of the theoretical is obtained if the reaction mixture is heated in sealed tubes at 240—250° for twenty to thirty hours. The *hydrochloride* of 2-aminopyridine is prepared by the usual methods, and is obtained in the form of an extremely deliquescent solid, melting at about 16°, and, after drying in a desiccator, containing 2H<sub>2</sub>O, which it loses at 105°. Di-2-pyridylamine forms slender, colourless needles, m. p. 95°. The specimen previously described (cf. above) melted at 84°, but on cooling solidified and melted at 95°; the substance thus appears to be polymorphous. The *hydrochloride* forms lustrous prisms, m. p. 115—116°, containing 3H<sub>2</sub>O (cf. however, A., 1916, **739**), which are slowly lost on drying. The *picrate* of the base forms needles, m. p. 225°. The *sulphate* forms hair-like needles, m. p. 248°.

G. A. R. K.

**The Investigation of 2:6-Diaminopyridine.** A. E. TSCHITSCHIBABIN and O. A. ZEIDE (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 522—533).—2:6-Diaminopyridine, prepared as before (A., 1915, i, 590), is shown to be a mono-acid base; like 2:6-dihydroxypyridine (Gattermann and Skita, A., 1916, i, 419), it couples with aromatic diazo-compounds. The action of nitrous acid on the diamine does not lead to the formation of a colouring matter corresponding with Bismarck brown, but to a 3-nitroso-compound.

The *hydrochloride* of the base is obtained in the form of very unstable white needles. The *sulphate*, (C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, forms yellow prisms. The *picrate* forms long, dark-yellow needles, m. p. 240°.

A *monoacetyl* derivative could not be obtained; the *diacetyl* compound, readily formed by the action of acetic anhydride on the base in benzene or glacial acetic acid, forms white, lustrous plates, m. p. 203°. The direct nitration of 2:6-diaminopyridine gives a very poor yield of the nitro-derivative, but the diacetyl compound is readily nitrated in the presence of concentrated sulphuric acid, giving a 70% yield of 3-nitro-2:6-diacetamidopyridine, light yellow needles, m. p. 192—193°; it appears to form salts with hydrochloric and sulphuric acids. The compound is readily deacetylated by hydrochloric acid, giving 3-nitro-2:6-diaminopyridine, lustrous yellow plates, m. p. 230° (blackens). The action of nitrous acid on 2:6-diaminopyridine under a variety of conditions, but best of all in the presence of acetic acid, leads to 3-nitroso-2:6-diaminopyridine, which crystallises in lustrous, ruby-red needles; it blackens and decomposes without melting when heated; it forms yellow salts with acids, and does not give Liebermann's nitroso-reaction. The mother-liquors from the preparation of this compound readily assume a green or blue coloration, probably due to the presence of readily oxidisable

hydroxypyridines. The nitroso-compound, on oxidation with hydrogen peroxide in ammoniacal solution, yields the nitro-compound described above. The reduction of the nitroso-compound with sodium hyposulphite or zinc dust does not lead to the desired triaminopyridine, owing to the extreme readiness with which the reduction product is oxidised to black colouring matters.

Benzenediazonium chloride couples with 2:6-diaminopyridine, yielding the compound  $C_{11}H_{11}N_5$ , orange-yellow needles, m. p.  $137^\circ$ , soluble in water with an orange colour, and in sulphuric or hydrochloric acid with a red colour. The solution in hydrochloric acid is decolorised by zinc dust, but rapidly assumes a green colour when exposed to the air.

With diazotised benzidine, a red compound,  $C_{22}H_{10}N_{10}$ , is produced which crystallises in lustrous, bronze-coloured plates and yields bluish-black, sparingly soluble salts with acids; it dissolves in sulphuric acid with an intense blue colour. G. A. R. K.

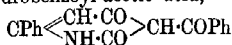
**6-Amino-2-methylpyridine.** O. A. ZEIDE (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 534—543).—The preparation of 6-amino-2-methylpyridine, first obtained by Tschitschibabin and Zeide (*A.*, 1915, i, 590) has been improved in details and is described. The compound is a mono-acid base the reactions of which are shown to be analogous to those of 2-aminopyridine (compare preceding abstracts). The pure base is a snow-white, crystalline mass, m. p.  $40^\circ$ , which is deliquescent. The following salts were prepared: the *hydrochloride* forms white needles; the *hydrobromide*, long, white prisms, m. p.  $149$ — $150^\circ$ ; the *hydriodide*, yellow prisms, m. p.  $162^\circ$ ; the *sulphate*, hard, colourless prisms; the *nitrate*, white needles, m. p.  $168^\circ$ ; the *picrate*, small, yellow needles, m. p.  $202^\circ$ ; *chloroplatinate*, flat, orange, rhombic prisms, m. p.  $209^\circ$ .

The *acetyl* compound, prepared by means of acetic anhydride in benzene solution, forms elongated, white prisms, m. p.  $90^\circ$ , readily soluble in water, alcohol, ether, or chloroform, sparingly soluble in cold petroleum. The *benzoyl* compound, prepared by the Schotten-Baumann method, forms hard, colourless prisms, m. p.  $90^\circ$ , from a mixture of benzene and petroleum; it is sparingly soluble in water and petroleum, and readily soluble in alcohol, benzene, chloroform, or ether.

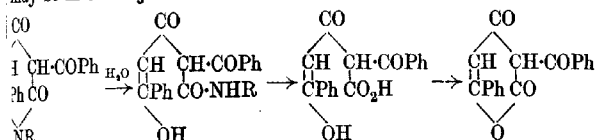
The action of nitrous acid on 6-amino-2-methylpyridine in hydrochloric acid solution leads to the formation, in 50% yield, of 6-chloro-2-methylpyridine, a colourless, mobile liquid with a sweet odour, readily miscible with organic solvents, b. p.  $183.5$ — $184^\circ/749$  mm. (*chloroplatinate*, red prisms insoluble in alcohol, blackens above  $208^\circ$ , decomposes above  $290^\circ$ ). 6-Hydroxy-2-methylaminopyridine is formed as a by-product in this reaction, and is separated from the chloro-compound owing to its solubility in alkalis; or it can be obtained by the action of nitrous acid on the amino-compound in the presence of sulphuric acid. It crystallises from a mixture of benzene and light petroleum in groups of needles, m. p.  $159^\circ$  (*picrate*, m. p.  $149.5$ — $150^\circ$ , light yellow needles from water, alcohol, or ethyl acetate; very soluble in acetone); the hydroxy-compound is identical with that prepared by Errera (*A.*, 1901, i, 43).

The nitration of the amine under the usual conditions leads to a 90% yield of 6-nitroamino-2-methylpyridine, slightly yellow needles from hot water or colourless crystals from alcohol, decomp. about 94°. The nitroamine is readily isomerised under the conditions previously employed (see preceding abstracts) to two isomeric nitro-compounds. The isomeride which is volatile in steam is assumed to be 5-nitro-6-amino-2-methylpyridine and forms delicate, light yellow needles, m. p. 141°. The isomeride which is not volatile in steam is taken to be 3-nitro-6-amino-2-methylpyridine; this compound is formed in greater amount than the 5-nitro-compound and is less soluble; it forms yellow leaflets, m. p. 188°. Both isomerides form colourless solutions in strong acids, and these solutions turn yellow on dilution; they are soluble in dilute alkalis but not in dilute acids. G. A. R. K.

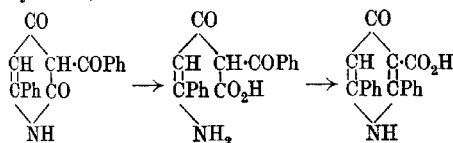
**The Lactam Derivatives of Dehydrobenzoylactic Acid.**  
P. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 251-259; cf. *ibid.*, 1915, 47, 645).—The reactions of some lactam derivatives of dehydrobenzoyl-acetic acid,



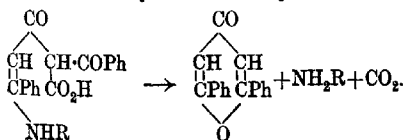
and its *N*-methyl derivative, with acids and strong and weak alkalis are explained as follows. With weak alkali both these substances are hydrolysed to an  $\alpha$ -pyrone derivative, as follows, where R may be H or CH<sub>3</sub>:



With strong alkalis, the free lactam forms 2:6-diphenylpyridone-3-carboxylic acid, as follows:



In the case of the *N*-methyl derivative, the methyl group is removed by hydrolysis, and the same product is then obtained as from the unsubstituted lactam. With strong acids, the reaction is as follows, where -R may be -H or -CH<sub>3</sub>:



R. T.

**The Methylation of Pyrrol Ketones.** B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 272—282).—1-Methyl-2-pyrrole methyl ketone, b. p. 199—201°/739 mm.,  $d_4^{25}$  1.0445,  $n_D^{25}$  1.5403, is obtained in 56% yield by heating the sodium salt of 2-pyrrol methyl ketone with methyl iodide in a sealed tube, whereas Ciamician and Dennstedt (A., 1885, 378) obtained only an 18% yield by acting on 1-methylpyrrole with acetic anhydride. 1-Methyl-2-pyrrole phenyl ketone, b. p. 299—301°/747 mm.,  $d_4^{25}$  1.1312,  $n_D^{25}$  1.6225, is prepared in 70% yield by the action of dimethyl oxalate on the sodium salt of 2-pyrrole methyl ketone. *Di-1-methyl-2-pyrrol ketone*, b. p. 305—307°/755 mm.,  $d_4^{25}$  1.1444,  $n_D^{25}$  1.6347, is prepared in the same way in 65% yield. At the same time, some *di-2-methyl-5-pyrrol ketone*, m. p. 192—197°, is produced. Other methods tried for the preparation of the di-1-methylpyrrol ketone did not give the desired product. The action of magnesium methyl iodide on 1-methyl-2-pyrrol phenyl ketone yields  $\alpha$ -methylpyrrol- $\alpha$ -phenyl  $\Delta^2$ -allene,  $\text{CHMe} \cdot \text{CPh} \cdot \text{C}_4\text{H}_9\text{NMe}$ , b. p. 281—283°/750 mm.,  $d_4^{25}$  1.0228,  $n_D^{25}$  1.5967. R. T.

**Relation between Absorption and Structure.** V. The **N-Phenylpyridinium Salts.** V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 190—205; cf. König, A., 1906, i, 109; 1911, i, 485).—Various 1-phenylpyridinium salts are reinvestigated and described. These are as follows: 1-Phenylpyridinium bromide, yellow needles, m. p. 155°, iodide, red crystals, m. p. 207°, chloride ( $\text{H}_2\text{O}$ ), white needles, m. p. 104—105°, chlorate, white plates with blue fluorescence, m. p. 214°. *o*-Iodophenylpyridinium bromide, yellow crystals, m. p. above 260°, iodide, yellow plates, m. p. 253°, chlorate, white crystals, m. p. 162°. *p*-Iodophenylpyridinium chloride, colourless crystals, m. p. above 260°, chlorate, colourless crystals, m. p. 213°. *m*-Iodophenylpyridinium bromide, colourless crystals, m. p. 189°, iodide, yellow crystals, m. p. 196—197°, chlorate, white plates, m. p. 146°. Tribromo-*m*-iodophenylpyridinium bromide, white crystals, m. p. above 260°. 5-Iodo-*o*-tolylpyridinium bromide, yellow crystals, with 1 molecule of water, m. p. 137—140°, iodide, orange-brown prisms, m. p. above 260°. 2-Hydroxy-1-phenylpyridinium chloride, yellow crystals, m. p. 210°, iodide, yellow crystals, m. p. 162°, chlorate, white needles, m. p. 154°, bromide, white needles, m. p. 128°.  $\beta$ -Hydroxy-*p*-iodophenylpyridinium chloride, white crystals, m. p. 200°, acid sulphate, yellow leaves, m. p. 147°. 1-*o*-Anisylpyridinium bromide, white crystals, m. p. 150°, iodide, yellow crystals, m. p. 153°, chloride ( $\text{H}_2\text{O}$ ), yellow crystals, m. p. 137.5°, chlorate, white crystals, m. p. 132°, hydrogen sulphate ( $\text{H}_2\text{O}$ ), yellow needles, m. p. 168°. *p*-Anisylpyridinium bromide, yellow crystals containing 1 molecule of alcohol of crystallisation, m. p. 123.5°, iodide, yellow crystals, m. p. 160°, chloride, white crystals, m. p. 100°, chlorate, white plates, m. p. 154°. *m*-Methoxyphenylpyridinium iodide, yellow needles, m. p. 122—123°, chlorate, white, faintly fluorescent needles, m. p. 113—114°.  $\beta$ -Naphthylpyridinium bromide, needles, m. p. 189°, iodide, yellow crystals, m. p. 201°, chloride, white crystals,

containing 1 molecule of alcohol of crystallisation, m. p. 100—103°, chlorate, colourless leaves, m. p. 192—193°. *o*-Phenetidylpyridinium bromide, needles, m. p. 195—196°, iodide, yellow needles, m. p. 186°. R. T.

**Derivatives of Indole.** SAJURO KURODA (*J. Pharm. Soc. Japan*, 1923, 131—142).—Applying Fischer's method for the synthesis of indole to many phenylhydrazones of ketones, the author has isolated the corresponding indole derivatives; except the product from menthone, these give a red coloration to a paper shavings moistened with hydrochloric acid. The process in general consists in heating a mixture of equal quantities of the hydrazone and zinc chloride at a suitable temperature.

**3-Benzyl-2-methylindole** prepared from benzylacetonephenylhydrazone, m. p. 59°, and zinc chloride by heating on the water-bath, forms long plates, m. p. 116°. **2-Methyl-3-propylindole**, prepared from methyl-butyl-ketonephenylhydrazone and zinc chloride, is a light, brownish-red oil, b. p. 195°/40 mm. **2-Methyl-3-isopropylindole**, prepared from methylisobutyl-ketonephenylhydrazone and zinc chloride, is a light yellow, viscous oil, b. p. 173°/15 mm. **2-Methyl-3-n-octylindole**, prepared from methyl-nonyl-ketonephenylhydrazone and zinc chloride at 100°, is a yellow oil, b. p. 230—235°/35 mm. **3-Benzyl-1:2-dimethylindole**, prepared from benzylacetonephenylmethylhydrazone (a reddish-brown oil) and zinc chloride at 150°, is a light yellow, viscous oil, b. p. 235°/35 mm., having slight green fluorescence. **1:2-Dimethyl-3-propylindole**, prepared from methyl-butyl-ketonephenylmethylhydrazone and zinc chloride at 100°, is a light reddish-brown oil, b. p. 187°/35 mm. **1:2-Dimethyl-3-n-octylindole**, an oil, b. p. 25—230°/36 mm., was prepared from methyl-nonyl-ketonephenylmethylhydrazone, and zinc chloride at 100°. Camphorphenylhydrazone, prepared by Balbiano's method (*A.*, 1886, 72, 808), boils at 210°/17 mm., and yields a hydrochloride, m. p. 151°, when hydrogen chloride is passed into its ethereal solution, without formation of aniline and camphorenonitrile (cf. Balbiano, *loc. cit.*). Its bromine compound,  $C_{16}H_{22}N_2Br_2$ , forms white needles, m. p. 186°. **Camphorindole** forms colourless plates, m. p. 94°, b. p. 210—215°/25 mm., and is prepared by heating a mixture of the hydrazone and zinc chloride at 150—180°. As a by-product, an isomeride of camphorphenylhydrazone,  $C_{16}H_{22}N_2$ , white plates, m. p. 201°, was isolated from the acid solution; it is not identical with the polycamphorphenylhydrazone of Cazeneuve (*Bull. Soc. chim.*, 1889, [iii], 1, 241). **Menthoneindole**,  $C_{16}H_{21}N$ , prepared from menthonephenylhydrazone and zinc chloride at 100°, forms colourless plates, m. p. 106°, b. p. 213°/20 mm. In the reaction there were also formed: aniline, and a base,  $C_{16}H_{23}N$ , a light yellow oil, b. p. 181°/18 mm.; it gives a *N*-benzoyl derivative, colourless prisms, m. p. 163°. K. K.

**The Action of Sodamide on Quinoline.** A. E. TSCHITSCH-BABIN and (Mlle) E. V. ZACEPINA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 553—557).—The preparation of 2-aminoquinoline by the

action of sodamide on quinoline (A., 1915, i, 591) has been reinvestigated in an endeavour to improve the yield of amino-compound, but without success. The main products of the reaction are *diquinoline*,  $C_{18}H_{14}N_2$ , and *diquinolyl*,  $C_{18}H_{12}N_2$ , the former being extremely readily oxidised to the latter, which is identical with the known 2:3-compound (Weidel, A., 1882, 69).

The following compounds are described: *2-Aminoquinoline*, purified by repeated crystallisation from water or regeneration from the picrate, melts at  $129^\circ$ ; the fractions of lower melting point which are obtained contain a little 4-aminoquinoline (hydrated form, m. p.  $69-70^\circ$ ; anhydrous form, m. p.  $153-154^\circ$ ). The *picrate*, sparingly soluble needles, m. p.  $255-256^\circ$ , and the *hydrochloride*, needles, m. p.  $225-227^\circ$ , were prepared. *Diquinoline* is isolated in the form of its *hydrochloride*, red needles, from hot water, readily oxidising in the air; the *base* obtained from it forms yellow leaflets, m. p.  $185^\circ$ . Thus it is not identical, but isomeric with the compound described by Claus (A., 1882, 215). Its salts with mineral acids have a bright red colour and are sparingly soluble; they are extremely readily oxidised to the colourless, readily soluble, salts of 2:3-diquinolyl which forms leaflets, m. p.  $175^\circ$ .  
G. A. R. K.

**The Action of Sodamide on *iso*Quinoline.** A. E. TSCHITSCHERBIN and (MILLE) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 543-548).—*iso*Quinoline reacts with sodamide in the presence of neutral solvents in the same way as pyridine and quinoline, an *aminoisoquinoline* being produced; the position taken up by the entering group is between the nitrogen and the benzene nucleus. The new compound, like those previously described, is a mono-acid base; by the action of nitrous acid, it is converted into the known *isocarbostyryl*, thus proving the constitution assigned to it.

*1-Aminoisoquinoline* is obtained in a yield amounting to 38% and forms silvery plates, m. p.  $123^\circ$ . The *picrate* has m. p.  $290-291^\circ$ . The *hydrochloride* forms needles, m. p.  $233-233.5^\circ$ . The *chloroplatinate*, thin, orange needles, does not melt below  $300^\circ$  and crystallises with  $1H_2O$ .

Diazotisation in presence of sulphuric acid leads to the formation of *isocarbostyryl*, almost white needles, m. p.  $206.5-207^\circ$  (cf. Fernau, A., 1893, i, 417); in the presence of hydrochloric acid some 1-chloro*iso*quinoline appears to be produced. G. A. R. K.

**Dihydro*iso*quinoline Derivatives.** M. HARTMANN and H. KAGI (U.S. Pat. 1437802).—Methyl  $\alpha$ -benzamido- $\beta$ -3:4-dimethoxyphenylpropionate, fine needles, m. p.  $104-105^\circ$ , obtained by the hydrogenation of methyl veratrylidenehippurate in methyl-alcoholic solution, when condensed at  $130-135^\circ$  with phosphorus oxychloride, yields methyl 6:7-dimethoxy-1-phenyl-3:4-dihydro*iso*quinoline-3-carboxylate, m. p.  $122.5^\circ$  after recrystallisation from methyl alcohol (*hydrochloride* and *hydrobromide*, yellow crystals). The free ester reacts with methyl iodide to give a 2-methiodide, which is converted by silver chloride into a 2-methochloride. Hydrogenation of methyl piperonylidenehippurate produces methyl

$\alpha$ -benzamido- $\beta$ -piperonylpropionate, brilliant needles, m. p. 126–127°, which on condensation gives methyl 6:7-methylenedioxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylate, colourless needles, m. p. 140.5°. Methyl  $\alpha$ -piperonylamino- $\beta$ -piperonylpropionate, glassy needles, m. p. 139–140°, yields on condensation methyl 6:7-methylenedioxy-1-mp-methylenedioxyphenyl-3:4-dihydroisoquinoline-3-carboxylate, m. p. 140–141° (hydrochloride, partly decomposed by water). Methyl 6:7-methylenedioxy-1-phenetyl-3:4-dihydroisoquinoline-3-carboxylate, prisms, m. p. 111°, is obtained by condensation of methyl  $\alpha$ -( $\beta$ -phenylpropionylamido)- $\beta$ -piperonylpropionate, m. p. 127°, formed by the hydrogenation of methyl  $\alpha$ -cinnamylamino- $\beta$ -3:4-methylenedioxyphenylacrylate, m. p. 192°. This compound is prepared by heating together equimolecular proportions of piperonal, cinnamylglycine, and sodium acetate and three molecular proportions of acetic anhydride and boiling the product with methyl alcohol and soda. The above compounds have therapeutic properties.

CHEMICAL ABSTRACTS.

**Vapour Pressure of Carbazole.** C. F. SENSEMAN and O. A. NELSON (*Ind. Eng. Chem.*, 1923, 15, 382–383).—A table of the vapour pressures of carbazole between 250° and 355° is given. The determinations were made on carefully purified samples (m. p. 244.8°) (A., 1922, i, 245). Carbazole has b. p. 354.76°, and not 351.5°, as stated in the literature. Interpolation formulæ are derived for the vapour pressures and latent heats of vaporisation:  $\log p = 24.2313 - 4570.3/T - 5.0288 \log T$  and  $L = 22799 - 13.0T$ , respectively. The values given for  $p$  are in good agreement with the observed values.

H. C. R.

**The Aldehyde Derivatives of the Rhodanines and their Fission Products. II.** LEON GENDELMAN (*Monatsh.*, 1923, 43, 537–543; cf. Andreasch, A., 1919, i, 96).—A continuation of previous work by Andreasch. Various substituted rhodanines have been prepared and their hydrolysis products examined and described: 5-cuminyldenerhodanine,  $\begin{matrix} \text{CS-S} \\ | \\ \text{NH-CO} \end{matrix} > \text{C:CH-C}_6\text{H}_4\text{-CHMe}_2$ ,

from cuminaldehyde and rhodanine, when hydrolysed by sodium amyl oxide in boiling amyl alcohol gave  $\alpha$ -thiol- $p$ -isopropylcinnamic acid,  $\text{C}_6\text{H}_4\text{Pr}^i\text{-CH:CH(C(SH)-CO}_2\text{H)}$ , fine yellow needles, which are oxidised by alcoholic iodine to the disulphide, yellow needles, m. p. 190°.

3-Phenyl-5- $p$ -chlorobenzylidenerhodanine,  $\begin{matrix} \text{CS-S} \\ | \\ \text{NPh-CO} \end{matrix} > \text{C:CH-C}_6\text{H}_4\text{Cl}$ ,

from phenylrhodanine and  $p$ -chlorobenzaldehyde, forms yellow needles, m. p. 148°. When hydrolysed by barium hydroxide it yields  $p$ -chloro- $\alpha$ -thiolcinnamic acid,  $\text{C}_6\text{H}_4\text{Cl-CH:CH(C(SH)-CO}_2\text{H)}$ , yellowish-white needles, m. p. 157°. 5- $p$ -Chlorobenzylidenethiohydantoin,  $\begin{matrix} \text{C(NH)S} \\ | \\ \text{NH-CO} \end{matrix} > \text{C:CH-C}_6\text{H}_4\text{Cl}$ , from thiohydantoin and  $p$ -chlorobenz-

aldehyde in acetic acid, forms yellow crystals which blacken at 230° without melting. 3-Phenyl-5- $p$ -tolylidenerhodanine, from  $p$ -tolualdehyde and phenylrhodanine, crystallises in yellow

needles, m. p. 136°, and is hydrolysed by barium hydroxide to  $\alpha$ -thiol-*p*-methylcinnamic acid,  $C_6H_4Me \cdot CH \cdot C(SH) \cdot CO_2H$ , yellow needles, m. p. 159°. It is oxidised by alcoholic iodine to the disulphide, yellow needles, m. p. 212°. When treated with alkali hydroxide and benzyl chloride, the thiol-acid yields  $\alpha$ -benzylthiol-*p*-methylcinnamic acid,  $C_6H_4Me \cdot CH \cdot C(S \cdot CH_2Ph) \cdot CO_2H$ , yellow needles, m. p. 134°. 5-mp-Dihydroxybenzylidenerhodanine,  $CS-S > C \cdot CH \cdot C_6H_3(OH)_2$ , from rhodanine and protocatechualdehyde, is a yellowish-brown powder, m. p. above 270°; its solutions are turned reddish-violet by alkalis and yellow by acids. Attempts to hydrolyse it by means of barium hydroxide or sodium amyloxide were unsuccessful. 3-Camphylrhodanine,  $C_{10}H_7 \cdot N \cdot CO \begin{smallmatrix} CS-S \\ > \end{smallmatrix} CH_2$ , is prepared by condensing camphylamine with carbon disulphide by means of aqueous alkali hydroxide to camphylthiocarbamate,  $C_{10}H_{17} \cdot NH \cdot CS_2Na$ , which is then condensed with chloroacetic ester to give 3-camphylrhodanine as a viscid, yellowish-red oil; this condenses with benzaldehyde to form 5-benzylidene-3-camphylrhodanine,  $C_{10}H_7 \cdot N \cdot CO \begin{smallmatrix} CS-S \\ > \end{smallmatrix} C \cdot CH \cdot C_6H_5$ , yellow needles, m. p. 49–50°. 5-*p*-Dimethylaminobenzylidene-3-camphylrhodanine, prepared in a similar manner from dimethyl-*p*-aminobenzaldehyde, forms orange-yellow needles, m. p. 129°. 5-*m*-Nitrobenzylidene-3-camphylrhodanine, from *m*-nitrobenzaldehyde, forms yellow needles, m. p. 126°. Camphylrhodanine condenses with isatin in acetic acid to form camphylrhodanine-2-indoleindigo [2-indoxylidene-3-camphylrhodanine],  $C_{10}H_7 \cdot N \cdot CO \begin{smallmatrix} CS-S \\ > \end{smallmatrix} C \cdot C \begin{smallmatrix} CO \\ \nearrow \\ NH \end{smallmatrix} > C_6H_4$ , brilliant deep red needles, m. p. 205–206°. F. A. M.

**Substitution in the Pyrazole Series. Halogen Derivatives of 3:5-Dimethylpyrazole.** GILBERT T. MORGAN and ISIDORE ACKERMAN (T., 1923, 123, 1308–1318).

**The Oxime of Mesoxamide (isoNitrosomalonomide) and some Allied Compounds. III. Ring Formation in the Tetra-substituted Series.** EDITH HILDA USHERWOOD and MARTHA ANNIE WHITELEY (T., 1923, 123, 1069–1089).

**The Action of Reducing Agents on some Polynitrodiphenylamines.** NICHOLAS MICHAEL CULLINANE and THOMAS CAMPBELL JAMES (*Aberystwyth Studies*, 1922, 4, 209–212).—Reduction of 2:4:6-trinitrodiphenylamine (picrylaniline) with alcoholic ammonium sulphide gives the known 1:3-dinitro-5:10-dihydrophenazine. It forms a diacetyl derivative,  $C_{16}H_{12}O_6N_4$ , yellow prisms, m. p. above 320°, and a dibenzoyl derivative,  $C_{26}H_{14}O_6N_4$ , yellow plates, m. p. 230° (decomp.). As an intermediate compound in the reduction, 2:4-dinitro-6-aminodiphenylamine was obtained, yellow leaflets, m. p. 176°. Reduction of picrylaniline with stannous chloride gives a black powder dissolving in concentrated sulphuric

acid with a violet colour. By reduction of picryl-*p*-toluidine with alcoholic ammonium sulphide, 6:8-dinitro-2-methyl-5:10-dihydrophenazine was obtained, bright yellow needles, m. p. above 340°. The constitution of this substance was confirmed by preparing it from picryltolylene-diamine (T., 1920, 117, 1273) by heating until nitrous fumes were no longer evolved. Reduction of picryl-*m*-toluidine with alcoholic ammonium sulphide appears also to give a dihydrophenazine derivative.

E. H. R.

**Micro-sublimation of Indigo.** KARL FIRSCHLE (*Biochem. Z.*, 1923, 136, 403—410).—The appearances obtained on micro-sublimation of a variety of indigo-containing materials, natural and synthetic, are described. Indirubin and indigotin both sublime in characteristic crystals and also crystallise from liquid paraffin in characteristic crystals.

H. K.

**isoIndigotin and Indine.** A. WAHL and W. HANSEN (*Compt. rend.*, 1923, 176, 1070—1072).—The identity of isoindigotin (A., 1909, i, 330, 735) with the indine first obtained by Laurent (*Ann. Chim. Phys.*, 1840, [iii], 3, 471) by the action of potassium hydroxide on disulphoisatide has been established by a comparison of the properties of the substances obtained by the two methods, and of their derivatives. The molecular formula of Laurent's product is definitely  $C_{16}H_{10}O_2N_2$ , the same as isoindigotin. Both substances give a brown compound with potassium hydroxide, and the original substance is in each case generated on dilution with water. Both furnished disulphonic acids, giving anhydrous barium salts, and silver, potassium, and sodium salts crystallising with  $2H_2O$ . The dimedisulphonic acid described by Schlieper (*Annalen*, 1861, 120, 4) is apparently erroneously so described, and was not obtained in the present research. On reduction with zinc dust and acetic acid, a leuco-compound having the formula  $C_{16}H_{12}O_2N_2$ , and forming white or pink crystals, m. p. 265°, was produced in each case, and its solution in alkali hydroxides rapidly reoxidised by air to isoindigotin.

G. F. M.

**Action of Sulphur Monochloride on Mercaptans.** GOPÂL CHANDRA CHAKRAVARTI (T., 1923, 123, 964—968).

**Ring Closure of Hydrazine-dithio- and -monothio-dicarbonyl-amides with Acetic Anhydride.** PRAPHULLA CHANDRA GUHA (*J. Amer. Chem. Soc.*, 1923, 45, 1036—1042).—Acetic anhydride converts hydrazinedicarbonylthioamide into a diacetyl derivative of 2:5-di-imino-2:3:4:5-tetrahydro-1:3:4-thiadiazole, from which it is easy to remove the acetyl groups; the reaction is also applicable to all alkyl and aryl hydrazinedicarbonylthioamides. Hydrazinedicarbonylmonothioamide, however, behaves differently; instead of losing either hydrogen sulphide or water and forming a di-imino-thiadiazole or -oxydiazole, it loses ammonia and gives a ketoinmino-thiadiazole.

The action of boiling acetic anhydride on hydrazinedicarbonylthioamide leads to 2:5-di-imino-3:4-diacetyl-2:3:4:5-tetrahydro-1:3:4-thiadiazole, white needles, m. p. above 315°, which is

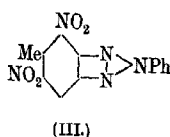
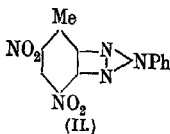
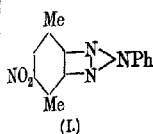
hydrolysed by means of concentrated hydrochloric acid to the *hydrochloride*, white needles, m. p. 241°, of 2:5-*di-imino*-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole*, m. p. 210—211°, yellow *picrate*, of high melting point. The following derivatives of the corresponding *dimethylamide* are described: *diacetyl* compound, white needles, m. p. 219°, free *base*, m. p. 180°, *hydrochloride*, m. p. 235°, *nitroso*-derivative, golden-yellow, m. p. 151°, yellow, crystalline *picrate*, m. p. 205°. The following derivatives of the *diallylamide* have been prepared: *acetyl* derivative, m. p. 113°, *hydrochloride*, and free *base*, m. p. 151°, also the following derivatives of the corresponding *dianilide*: *acetyl* derivative, m. p. 224°, free *base*, m. p. 247°. Similarly, the following derivatives of the di-*p*-toluidide are obtained: *diacetyl* compound, m. p. 235°, free *base*, m. p. 249—250°, and of the *monoanilide*: free *base*, dull, yellow leaflets, m. p. 215°, *hydrochloride*, m. p. 144°, yellow *picrate*, m. p. 226°, *diacetyl* derivative, m. p. 144°. *p*-Bromophenylhydrazinedicarbothionamide, m. p. 213°, is prepared by boiling for three to four hours a mixture of one molecular proportion of hydrazine sulphate dissolved in the minimum amount of warm water, and one molecular proportion of sodium carbonate and two molecular proportions of *p*-bromophenylthiocarbimide. It gives the following derivatives of the *mono-p*-bromoanilide: free *base*, m. p. 241°, *diacetyl* derivative, m. p. 229°. *m*-Chlorophenylhydrazinedicarbothionamide, m. p. 170°, is prepared in a similar manner, and gives the impure *diacetyl* derivative from which the free *base*, m. p. 186—187°, is obtained.  $\alpha$ -Naphthylhydrazinedicarbothionamide, m. p. 265°, gives, in the same way, the free *base*, m. p. 275—276°, and the *diacetyl*-derivative, m. p. 270°. The action of boiling acetic anhydride on hydrazinemonothiodicarbonamide leads to the *diacetyl* derivative, m. p. 295°, of 5-*imino*-2-*keto*-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole*, m. p. 240°, *hydrochloride*, m. p. 107—108°. W. S. N.

**Benzbisthiazoles. III.** STEPHEN RATHBONE HOLDEN EDGE (T., 1923, 123, 1011—1014).

**Dyes of the Aurin Type. I.** HARRY BAINES and JOHN EDMUND DRIVER (T., 1923, 123, 1214—1218).

**Certain o-Nitrohydrazo-compounds.** MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1923, 53, i, 165—174).—It has been found previously (A., 1918, i, 552) that the action of gaseous hydrogen chloride on methyl- or ethyl-alcoholic solutions of certain *o*-nitrohydrazo-compounds yields intense wine-red or carmine colorations. It is now found that this reaction may be extended and employed for the identification of products formed by the action of phenylhydrazine on aromatic nitro-compounds containing labile groupings such as halogens, alkyl-oxy-, or nitro-groups, etc. The ortho-position to the labile group being usually occupied by a nitro-group, the primary product of this reaction is the *o*-nitrohydrazo-compound, but under certain conditions derivatives of 2:1:3-benzotriazole or phenyl- $\psi$ -aziminobenzene are obtained (cf. Kehrman and Messinger, A., 1892, 889). The compound, described as 3:5-

dinitroso-2-benzeneazo-*p*-xylene, m. p. 185° (A., 1920, i, 98), must, indeed, be regarded as the 2:1:3-benzotriazole derivative of formula I and that described as 6-nitro-2:4-dinitroso-3-benzene-azotoluene, as the dinitro-2-phenylmethyl-2:1:3-benzotriazole of formula II or III:



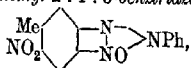
The products formed by the action of gaseous hydrogen chloride on some *o*-nitrohydrazo-derivatives in alcoholic solutions must be considered as azimino-oxides or azonitroso-derivatives, containing,

not the grouping  $\text{NO}\cdot\dot{\text{C}}\cdot\dot{\text{C}}\cdot\text{N}\cdot\text{NR}$ , but either  $\begin{array}{c} \cdot\text{N}\cdot \\ \diagup \quad \diagdown \\ \text{NO} \end{array}$  or  $\begin{array}{c} \cdot\text{N}\cdot \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ .

When, however, the action of phenylhydrazine or one of its derivatives with substituents in the nucleus on a nitro-compound with a labile group yields, not an *o*-nitrohydrazo-compound, but a derivative of phenyl-2:1:3-benzotriazole, no red coloration is given by the gaseous hydrogen chloride reaction. In some cases, gaseous hydrogen chloride in ethyl- or methyl-alcoholic solution is not a suitable agent for the formation of azonitroso-compounds, as it acts on these in a somewhat complicated manner, especially when its action is prolonged and the temperature is not duly regulated.

As regards the cause of the red coloration formed by the nitrohydrazo-compounds with the gaseous hydrogen chloride, two suggestions are made. It may be due to the formation of an additive compound of the acid with the intermediate nitrosoazo-compound,  $\cdot\text{N}\cdot\text{N}\cdot\dot{\text{C}}\cdot\dot{\text{C}}\cdot\text{NO}$ , or of a more complex compound (cf. Jacobson, Bartsch, Loeb, and Steinbreck, A., 1909, i, 681). The second suggestion, which is supported by Jacobson's results (1892—1909; also A., 1922, i, 589), is that part of the hydrazo-compound reacts with the gaseous hydrogen chloride, giving rise to the corresponding azo-compound, the two hydrogen atoms thus eliminated causing fission of another molecule of the hydrazo-compound with formation of two molecules of primary amine. A similar reaction was observed by Andrae (A., 1880, 466).

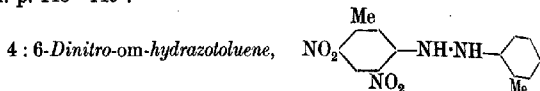
5-Nitro-2-phenyl-6-methyl-2:1:3-benzotriazole 3-oxide,



prepared by treating 2:4-dinitro-5-methylhydrazobenzene (A., 1918, i, 552), either in hot alcoholic solution with a few drops of 15% sodium hydroxide solution, or in a reflux apparatus with glacial acetic acid, or in alcoholic solution with gaseous hydrogen chloride solution, forms pale yellow, flat, silky needles, m. p. 155—156°.

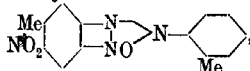
4 : 6-Benzeneazo-4 : 6-dinitro-*m*-toluene,  $C_8H_7Me(NO_2)_2 \cdot N \cdot NPh$ , obtained by oxidising benzenehydrazo-2 : 6-dinitro-*m*-toluene in alcoholic solution by means of freshly precipitated mercuric oxide, crystallises in brick-red lamellæ, m. p. 117—118°.

Benzenazo-2 : 4-dinitro-*m*-toluene forms reddish-yellow lamellæ, m. p. 148—149°.

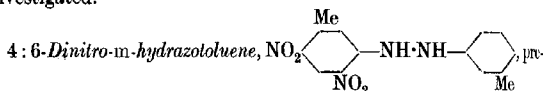


prepared by the interaction of  $\gamma$ -trinitrotoluene and *o*-tolylhydrazine, crystallises in lustrous, orange-red lamellæ, m. p. 151—152° (decomp.), dissolves in concentrated sulphuric acid giving a red solution, and in alcoholic solution yields a dark red coloration with alkali.

6-Nitro-2-*o*-tolyl-5-methyl-2 : 1 : 3-benzotriazole N-oxide,

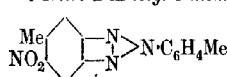


obtained from the preceding compound by means of either 25% potassium hydroxide solution or gaseous hydrogen chloride, forms yellow needles, m. p. 142—143°, and dissolves slowly in cold, concentrated sulphuric acid to a yellow solution. When prepared by means of hydrogen chloride, it is accompanied by a garnet-red, halogenated compound, m. p. above 220°, which has not been investigated.



pared from  $\gamma$ -trinitrotoluene and *m*-tolylhydrazine, crystallises in orange-yellow needles, m. p. 165—166° (decomp.), forms a dark red solution in concentrated sulphuric acid, and gives a red coloration with alkali in alcoholic solution.

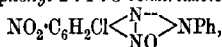
6-Nitro-2-*m*-tolyl-5-methyl-2 : 1 : 3-benzotriazole (annexed formula),

 prepared from  $\gamma$ -trinitrotoluene and *m*-tolylhydrazine, forms small, golden-yellow prisms, m. p. 150—151°; the N-oxide crystallises in pale yellow needles, m. p. 181—182°, and gives a yellow coloration with concentrated sulphuric acid.

6-Nitro-2-*p*-tolyl-5-methyl-2 : 1 : 3-benzotriazole N-oxide,

$C_{14}H_{12}O_3N_4$ , crystallises in lustrous, yellow lamellæ with a greenish-yellow reflection, m. p. 186—187°.

6-Chloro-5-nitro-2-phenyl-2 : 1 : 3-benzotriazole N-oxide,



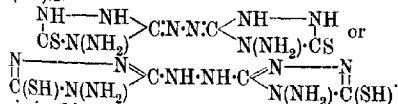
prepared from 5-chloro-2 : 4-dinitrohydrazobenzene, either by boiling it with glacial acetic acid or by saturating its alcoholic

solution with gaseous hydrogen chloride, forms golden-yellow needles, m. p. 195—196°. When reduced by means of hydrazine hydrate, this compound yields a product with the same melting point as Zincke and Scharff's phenyl- $\psi$ -aziminonitrochlorobenzene [A., 1910, i, 140], namely, 196°. T. H. P.

**Action of Diazomethane on Xanthosine.** P. A. LEVENE (*J. Biol. Chem.*, 1923, 55, 437—442).—The velocity of hydrolysis of the hydrogenated pyrimidine nucleoside indicates that the pentose radicle is attached to a nitrogen atom of the base. Assuming that the same mode of attachment exists in all nucleosides, the structure of those containing a pyrimidine base follows immediately. In the case of the purine nucleosides, however, alternative positions of attachment are possible. It is now shown that, in xanthosine, the ribose molecule is attached to the nitrogen atom in position 1 of the base. Thus, methylation of xanthosine with diazomethane yielded an amorphous *dimethyl* derivative,  $[\alpha]_D^{20} - 28^\circ$ , together with caffeine, and, when the methylation was continued for eight hours, tetramethyluric acid. The production of the last two compounds is attributed to the hydrolytic and oxidising actions of diazomethane. When hydrolysed by dilute acid, dimethyl-xanthosine gave theophylline; hence the 1- and 3-positions of the purine base are free in the nucleoside, thus leaving only position 7 as the point of attachment of the pentose. The yield of theophylline was small owing to considerable formation of melanin. E. S.

**Ring Closure with Hydrazinedicarboxamides containing Sulphur. III. The Action of Hydrazine on Hydrazinedicarbonylthioamide.** F. ARNDT and FRANZISKA BIELICH (*Ber.*, 1923, 56, [B], 809—817; cf. Arndt and Milde, A., 1921, i, 813; Arndt and Tschenschner, A., 1922, i, 375).—The action of hydrazine on hydrazinedicarbonylthioamide has been described by Purgotti and Vigano (A., 1902, i, 322), who have isolated a product which they regard as dithio-*p*-urazine,  $S_2C \begin{smallmatrix} \text{NH-NH} \\ \text{NH-NH} \end{smallmatrix} > CS$ . Since

the constitution ascribed to this compound seems doubtful to the authors, they have re-examined the reaction with different results and have isolated the amphoteric 4-amino-3-iminothiourazole,  $NH_2 \cdot N \begin{smallmatrix} \text{C}(\text{NH}) \cdot \text{NH} \\ \text{CS} \text{---} \text{NH} \end{smallmatrix}$ , 4-aminodithiourazole,  $NH_2 \cdot N \begin{smallmatrix} \text{CS} \cdot \text{NH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$  or  $NH_2 \cdot N \begin{smallmatrix} \text{C}(\text{SH}) \cdot \text{N} \\ \text{C}(\text{SH}) \cdot \text{N} \end{smallmatrix}$ , and (probably) 4 : 4-diaminohydrazothiothiourazole,



4-Aminoiniminothiourazole crystallises in irregular leaflets, m. p. 240—242° (decomp.). It is soluble in alkalis, ammonia, and mineral acids, but not in acetic acid. It gives a colourless *nitrate*, m. p. 53° (decomp.), and a *methyl* ether. It reacts with benzaldehyde in hydrochloric acid solution to give the *benzylidene* compound,

$\text{CHPh:N-N} \begin{array}{l} \swarrow \text{C}(\text{NH})\cdot\text{NH} \\ \text{CS} \text{---} \text{NH} \end{array}$ , lustrous, pale yellow prisms, m. p. 274°

after previous darkening (the corresponding *S-methyl ethyl* has m. p. 242° after softening at 235°).

4-Aminodithiourazole crystallises in small, colourless needles, m. p. 228° (decomp.) after softening at 225°. It is oxidised by ferric chloride in hydrochloric acid solution to the corresponding disulphide,  $(\text{C}_2\text{H}_2\text{N}_4\text{S}_2)_2$ , a pale yellow precipitate, m. p. (indefinite) 214° (decomp.). It gives a silver salt,  $\text{C}_2\text{H}_2\text{N}_4\text{S}_2\text{Ag}_2$ , and a barium salt,  $(\text{C}_2\text{H}_3\text{N}_4\text{S}_2)_2\text{Ba}\cdot 4\text{H}_2\text{O}$ . The benzylidene derivative forms pale yellow crystals, m. p. 136° after previous softening. The amino-compound is converted by benzyl chloride and alcoholic potassium hydroxide solution into the corresponding dibenzyl ether,  $\text{NH}_2\cdot\text{N} \begin{array}{l} \swarrow \text{C}(\text{S}\cdot\text{C}_6\text{H}_7)\cdot\text{N} \\ \text{C}(\text{S}\cdot\text{C}_6\text{H}_7)\cdot\text{N} \end{array}$ , matted needles, m. p. 147°.

4:4'-Diaminohydrazothiazole (?) crystallises in long, colourless, or pale-yellow needles. It has m. p. 207—225° after previous softening, the indefiniteness appearing to be due to tautomeric or stereochemical change, and not to the presence of impurity in the material. It is a powerful reducing agent, but its smooth conversion into a disulphide could not be effected by means of ferric chloride or iodine solution. It gives an unstable silver salt. The benzylidene compound crystallises in small needles, m. p. 215° (decomp.). The benzyl ether, leaflets, m. p. 214° (decomp.), yields salts with the mineral acids of which the nitrate, m. p. 132°, is the most sparingly soluble. The benzylidene derivative of the benzyl ether forms small needles, m. p. 136—137°; it yields a hydrochloride, m. p. 181°.

H. W.

**Action of Hydroxylamine and of Dihydroxyammonia on certain Nitroso-derivatives.** A. ANGELI and ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 151—153).—From the analogies in behaviour shown by two groups when directly united and when occupying ortho- or para-positions in an aromatic nucleus (A., 1917, i, 452; 1920, i, 665), it is to be expected that aromatic compounds of the form  $\text{NHR}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ,  $\text{NHR}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$ , or  $\text{NR}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{OH}$  would, in some reactions, behave similarly to the hydrazines or diazo-hydrates. When treated with nitrous acid, amides of the first of the above forms give, not the corresponding diazonium salts, but compounds of the probable formula  $\text{NR}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2$  (cf. Ikuta, A., 1888, 467), which may be regarded also as derivatives of diazoiminoquinone,  $\text{NR}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}$ . Further, since diazonium hydroxides are converted by the action of hydroxylamine into the corresponding azides,  $\text{R}\cdot\text{N}_2\cdot\text{OH} + \text{NH}_2\cdot\text{OH} = \text{R}\cdot\text{N}=\text{N}=\text{N} + 2\text{H}_2\text{O}$ , the action of this reagent on nitroso-derivatives of the type  $\text{NHR}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$  should furnish either diazoiminoquinone or a very simple derivative of it. This is actually found to be the case.

The action of hydroxylamine on *p*-nitrosodiphenylamine in alkaline solution yields a compound,  $\text{C}_{12}\text{H}_{10}\text{N}_4$ , which forms large, pale brown crystals, m. p. 71°, and on reduction with tin and

hydrochloric acid gives the amine,  $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . The formula  $\text{NH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$  being unlikely, this compound has probably the structure  $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{N}$  or  $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NH}$ , the diazo-compound,  $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$ , first formed undergoing reaction with a second molecule of the hydroxylamine.

Similarly, the action of hydroxylamine on the nitroso-compound,  $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$ , yields a crystalline compound, m. p.  $52^\circ$ . Both these compounds, for which the name *photo-azides* is suggested, exhibit sensitiveness towards light resembling that of silver salts. Paper moistened with a dilute benzene solution of the phenyl derivative and exposed to light rapidly turns violet and then black; with the methyl derivative first a red and afterwards a violet coloration is obtained.

Dihydroxyammonia, obtained from benzosulphohydroxamic acid and an alkali, acts readily on *p*-nitrosodiphenylamine in alkaline solution, yielding an acid compound, which forms deep yellow crystals, m. p.  $74^\circ$ , and undergoes rapid alteration when either heated or exposed to light.

T. H. P.

**Certain Polypyrrroles.** ANTONIO PIERONI and ALDO MOGGO (*Gazzetta*, 1923, 53, i, 120—135).—Part of the work here described has been already published (A., 1922, i, 766). Besides *p*-bromobenzenediazoxycarboxylamide, naphthalene- $\beta$ -azoxycarboxylamide may serve as a reagent for the pyrrole nucleus, with which it forms pyrrolineazo- $\beta$ -naphthalene and pyrrolinebisazo- $\beta$ -naphthalene (cf. Fischer and Hepp, A., 1886, 1041). The action of *p*-bromophenyldiazonium chloride on iodole or on heptaiododipyrrol (A., 1922, i, 763) yields bis-2 : 5-*p*-bromobenzenediazodi-iodopyrrole.

Naphthalene- $\beta$ -azoxycarboxylamide,  $\text{C}_{10}\text{H}_7\cdot\text{NO}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , prepared in the ordinary way from  $\beta$ -naphthylamine, crystallises in orange-yellow, silky needles, m. p.  $178^\circ$ , and with  $\beta$ -naphthol and a few drops of potassium hydroxide gives a violet solution which, when heated, becomes red and yields a red precipitate of  $\beta$ -naphthylazo- $\beta$ -naphthol.

Bis-2 : 5-*p*-bromobenzenediazodi-iodopyrrole,  $\begin{matrix} \text{ClC}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Br}) \\ \text{ClC}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Br}) \end{matrix} > \text{NH}$ ,

forms red crystals and decomposes, with liberation of iodine, at  $259^\circ$ .

T. H. P.

**Azo-dyes of the 2-Pyridine Series.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 512—519).—Sodium pyridine isodiazoxide (A., 1916, i, 224, and this vol., i, 597, 598) reacts in alcoholic solution with certain phenols and aromatic amines, giving true azo-dyes. The coupling proceeds very slowly, but is greatly accelerated by passing a slow stream of carbon dioxide through the liquid; indeed, no condensation takes place with amines if the presence of carbon dioxide is excluded. Curiously enough, no condensation product could be obtained with the sodium salt of *G* acid (sodium  $\beta$ -naphthol-6 : 8-disulphonate). The attempts to condense  $\alpha$ -aminopyridine with nitrosonaphthol and nitroso-dimethylaniline were also unsuccessful. Azo-dyes containing a

pyridine nucleus as first component are much deeper in colour than the corresponding benzene derivatives; whilst as a second component the pyridine nucleus has little effect on the colour. The simple dyes obtained do not appear to be very stable.

The following compounds are described: *2-Pyridineazo- $\beta$ -naphthol*, orange-red needles, m. p.  $137^{\circ}$ , obtained in 40% yield in addition to some 2-ethoxypyridine; insoluble in water and cold alkalis, soluble in dilute acids, dissolves in concentrated sulphuric acid with a dark purple colour; the *hydrochloride* forms red needles. *2-Pyridineazo- $\alpha$ -naphthol* appears to exist in two isomeric forms, one consisting of red needles with a green reflex, giving a dirty violet solution in sulphuric acid, and another which forms dark needles giving orange-red solutions in acids or alkalis. *2-Pyridine-azoresorcinol* is obtained partly in the form of its *mono-sodium* salt, an orange powder containing one molecule of water of crystallisation, and partly as its *hydrochloride*, which is also obtained by treating the sodium salt with hydrochloric acid, red, flattened needles containing  $2\text{H}_2\text{O}$ . The *base* can be liberated from the sodium salt by means of carbon dioxide and forms an orange, crystalline powder (prisms) which swells and blackens at  $186$ – $188^{\circ}$  and gives orange solutions in acids or alkalis. *2-Pyridine-3-azo-2:6-diaminopyridine* forms brownish-red crystals containing alcohol of crystallisation which is readily lost on keeping, the substance then melting at  $167^{\circ}$ . It dissolves sparingly in sulphuric acid, giving a greenish-yellow solution. G. A. R. K.

**Action of Iodine on some  $\alpha$ -Substituted Semicarbazides and its Application to their Estimation.** A. DORCET (*J. Pharm. Chim.*, 1923, [viii], 27, 361–365).—Iodine reacts with  $\alpha$ -phenylsemicarbazide otherwise than with semicarbazide itself; no nitrogen is liberated, but two hydrogen atoms are eliminated as hydrogen iodide and phenylazocarboxylamide,  $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , melting at  $114^{\circ}$ , is formed. The latter forms, with an excess of iodine, an unstable additive compound which separates in small, bronze needles, but is readily dissociated by solvents and loses its iodine when treated with sodium thiosulphate. The estimation of 1-phenylsemicarbazide may be carried out by adding 50 c.c. of  $N/10$ -iodine to a solution of 0.2 g. of the substance in 10 c.c. of alcohol containing 1 g. of sodium acetate. After keeping the mixture for ten minutes 50 c.c. of  $N/10$ -sodium thiosulphate are run in and the excess is titrated back with  $N/10$ -iodine, using starch as indicator. Every 2 atoms of the original iodine used correspond with 1 mol. of phenylsemicarbazide. *m*-Benzamidosemicarbazide behaves exactly as the above, giving *m*-benzamidazocarboxylamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , which differs from phenylazocarboxylamide in being insoluble in ether, chloroform, or benzene. The azo-derivative is a stable compound, melting at  $186^{\circ}$  and giving an unstable additive compound with iodine. W. T. K. B.

**Cataphoresis of Proteins.** THE. SVEDBERG and ERIC R. JETTE (*J. Amer. Chem. Soc.*, 1923, 45, 954–957).—A method is described by which the rate of migration of a protein particle under

the influence of an electric field may be experimentally determined. The method depends on the fact that under the illumination of ultra-violet light, proteins fluoresce. This fluorescence may be easily photographed and the position of the boundaries of the protein sol measured on the photographic plate. Photographs are included in the paper showing qualitatively the effect of changing the hydrogen-ion concentration of a 0.3% egg-albumin sol on its rate of migration.  
J. F. S.

**The Decomposition of Proteins. II.** N. TROENSEGAARD (*Z. physiol. Chem.*, 1923, 127, 137—185).—Proteins, gelatin, rhadin, and casein are acetylated when heated with acetyl chloride in acetic acid solution. The acetyl proteins are reduced with sodium and amyl alcohol and the products fractionated. The chief products appear to be heterocyclic compounds, probably pyrrole derivatives. Aliphatic amines and amino-alcohols appear to be absent.  
W. O. K.

**Comparative Value of the Dialysis Reaction (Abderhalden) and the Reaction with *Bacterium coli* for the Detection of Proteolysis.** E. WOLLMAN and (MME) E. WOLLMAN (*Bull. Soc. Chim. biol.*, 1923, 5, 253—257).—The authors' method (*Compt. rend. Soc. Biol.*, 1919, 82, 1263), in which the tryptophan present in the peptones produced by proteolysis is converted into indole (detected by Ehrlich's reagent) by the action of *B. coli*, gives more regular results and is more sensitive than Abderhalden's dialysis method.  
E. S.

**Investigation of Formaldehyde-protein. A Case of Divergence from the Usual Characteristics of a Transition. Mechanism of Gel Formation.** L. REINER and A. MARTON (*Kolloid Z.*, 1923, 32, 273—279).—Formaldehyde-protein has been prepared from the sera of rabbits, horses, cows, and guinea-pigs and the physical properties of the product have been examined. The results show that the change in properties which generally indicate increased or decreased stability of the product do not all point in the same direction. The stability towards heat, and the reduction of the tendency to coagulate on the addition of albumin indicate an increased stability, whilst the increased sensitiveness towards salts, the more pronounced Tyndall cone, and the decreased electrical conductivity indicate a coagulation or at least a decreased stability of the complex compound over that of the original protein.  
J. F. S.

**The Action of Proteins and Blood-serum on Colloidal Gold Solution and its Quantitative Interpretation.** PAUL REZNIKOFF (*J. Lab. Clin. Med.*, 1922, 8, 92—103).—Serum-albumin, euglobulin, and pseudoglobulin, tested against colloidal gold solution, gave characteristic curves dependent on the concentration. Contrary to Fischer, the author finds that serum-albumin has a distinct precipitating effect on colloidal gold in certain concentration. Howe's method for isolating the globulins was found not to be accurate.  
CHEMICAL ABSTRACTS.

**Sensitisation of Salts by Globulin as the Cause of the Coagulation of Gold [Sols] by Globulin Solutions.** G. HEINRICH FISCHER and A. FODOR (*Kolloid Z.*, 1923, 32, 279—284).—The precipitation of gold sols by alkaline globulin solutions and by similar solutions containing 0.4% of sodium chloride has been investigated for various hydrogen-ion concentrations. The experiments indicate that with increasing hydration of the globulin the coagulation is retarded. But it is remarkable that coagulation is not entirely absent in solutions of hydrogen-ion concentration of the order  $10^{-12}$  when treated with globulin free from or poor in sodium chloride, whereas with albumin solutions in which the albumin is present as enhydrates (A., 1922, i, 691) and is strongly hydrated there is no increase in the size of the gold particles.

J. F. S.

**Colloid Chemistry of Yeast Proteins.** HEINRICH LÜBKE and KARL SCHUSTER (*Kolloid Z.*, 1923, 32, 334—337).—The yeast proteins, zymocasein and cerevesin, have been separated from yeast, the former by treating the liquor from compressed yeast with 20% acetic acid until the filtrate shows no further precipitation. This occurs at  $p_H=4.0-4.5$ . The precipitate is pressed, washed with faintly acidified water, and dialysed under toluene against water until the acid reaction disappears. The filtrate from the zymocasein is treated with sodium acetate and the cerevesin salted out with ammonium sulphate. The two proteins have been investigated with respect to their chief colloidal properties. The isoelectric point of cerevesin is found to be  $2.6 \times 10^{-5}$  from measurements of its coagulation by alcohol, and by heat, its surface tension, and its cataphoresis. The values of these constants show that this vegetable protein is to be grouped with the known animal and plant proteins. The tendency of zymocasein to swell in acid and acidified solutions of neutral salts has been investigated, and a far-reaching analogy with animal casein found. Zymocasein therefore belongs to the group of phosphorus-containing proteins (casein and vitellin).

J. F. S.

**Collargol.** A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 604—607; cf. A., 1917, i, 98; this vol., i, 492).—The addition of sodium chloride to a solution of collargol in quantities insufficient to precipitate the latter causes the gradual formation of a deposit of silver chloride in a colloidal form; the reaction is  $2Ag + 2NaCl + O + H_2O = 2AgCl + 2NaOH$ . This reaction is responsible for the deterioration of samples of solid collargol when these are not kept protected from air and moisture. Potassium iodide produces an analogous result, colloidal silver iodide being deposited. Silver chloride is shown to have a peptising action on collargol.

G. A. R. K.

**The Influence of Electrolytes on the Coagulation of Collargol by Acetic Acid.** ALEXEI FEDOROVITSCH GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 442—448).—Various inorganic salts are added singly and in pairs, in various quantities and pro-

portions, to solutions of colloidal silver, and acetic acid is then added until coagulation occurs. The amount of acid which needs to be added depends, not only on the quantity of the salts present, but also on the nature of the component salts of each pair. When the mixtures are added in small quantity, their mutual influence is negligible, whilst with large quantities, the activity of each salt may be neutralised. When intermediate quantities of mixtures are added, the effect is largely the sum of the effects of the components.

R. T.

#### The Proteic Acids of Urine. II. Antoxyproteic Acid.

S. EDLBACHER (*Z. physiol. Chem.*, 1923, 127, 186—189; cf. A., 1922, i, 692, 883).—Antoxyproteic acid contains only a small quantity of nitrogen titratable by formol (3.69%, excluding that which can be distilled as ammonia), but on hydrolysis yields a relatively high percentage of mono-amino-acids (37.10%), and also contains histidine, arginine, and lysine. It therefore appears to be of the nature of a polypeptide.

W. O. K.

**Precipitation Forms of Casein.** FRITZ LOEBENSTEIN (*Kolloid Z.*, 1923, 32, 264—272).—The significance of the various forms in which casein is precipitated in connexion with digestion is discussed. The conditions under which the various forms are produced have been investigated in the case of calcium caseinate solutions. Precipitation has been effected in the presence of hydrochloric acid of physiological concentrations and also in the presence of carbohydrates (lactose, maltose, sucrose, and dextrin), salts (sodium chloride and hydrogen carbonate, potassium chloride, citrate, phosphate, and sulphate, calcium citrate and phosphate and magnesium phosphate), albumin and ferments (pepsin and rennin), and the forms produced have been investigated. Hydrochloric acid is shown to have a marked effect on the solution of the casein. Calcium caseinate solutions give no precipitate in the presence of 0.2—0.3% hydrochloric acid; lower and higher concentrations of hydrochloric acid produce increasingly large precipitates, which differ considerably in their nature and in the time required for their formation. The addition of sugars prevents the precipitation over the whole concentration range of hydrochloric acid from 0.35 to 0.55%. Albumin has much the same action as the sugars, that is, it hinders precipitation and aids solution. The salts mentioned above, when present in physiological quantities, increase the precipitation over the whole range of hydrochloric acid concentrations. Pepsin does not affect the precipitation by hydrochloric acid, whilst rennin accelerates both the precipitation and the solution of casein.

J. F. S.

**The Combination between Oxygen and Hæmoglobin, and the Criteria of Adsorption.** N. K. ADAM (*Nature*, 1923, 111, 496—497).—The question is discussed whether the attraction of hæmoglobin for oxygen, which appears to be a localised property of the hæmoglobin particles, is correctly regarded as an adsorption phenomenon, even although the amount of oxygen taken up at

different pressures can be fairly accurately represented by the "adsorption isotherm." The author prefers to regard a process as being rightly classified as adsorption only if the substance taken up by the surface continues to be taken up until the whole surface is uniformly covered. Probably only a very small part of the surface of the hæmoglobin particles can be actually covered by oxygen when combination ceases at the stage of oxy-hæmoglobin. All cases of adsorption, from a gaseous phase, or from solution, on plane or nearly plane interfaces are compatible with the definition, whilst it is also probably applicable to those of adsorption on colloidal surfaces.

A. A. E.

**Adsorption and Hæmoglobin.** (SIR) W. M. BAYLISS (*Nature*, 1923, 111, 666—667; cf. Adam, preceding abstract).—The fact that when hæmoglobin is fully saturated with oxygen, the oxygen is taken up in the proportion of one molecule to each atom of iron in the hæmoglobin molecule does not exclude the possibility of adsorption at local foci, nor does an explanation based on true chemical combination account also, for example, for the greater affinity of hæmoglobin for carbon monoxide than for oxygen. It is pointed out that hæmoglobin under most conditions exists in the form of colloidal aggregates, so that the possibility of the intervention of surface phenomena must be considered. Adam's (*loc. cit.*) criterion of adsorption is briefly criticised, in that it appears to neglect cases in which two or more substances are adsorbed simultaneously.

A. A. E.

**The Triphosphonucleic Acid of Thannhauser and Dorf-müller.** R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1923, 127, 67—79).—It is concluded that the triphosphonucleic acid described by Thannhauser and co-workers (*A.*, 1914, i, 1015; 1916, i, 522; 1918, i, 47, 316; 1920, i, 895; 1921, i, 201) does not exist.

W. O. K.

**The Structure and Properties of Chondrin and of Hydrogen Chondroitin Sulphate (a New Method for the Preparation of Hydrogen Chondroitin Sulphate).** M. RAKUZIN and (MILLER) EK. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 200—207).—A solution of chondrin in water is decomposed by 2% aluminium hydroxide into hydrogen chondroitin sulphate, which remains in solution, whilst the chondrin residue is adsorbed in the colloid. When 5% of the latter is present in the solution, the reaction proceeds in two stages; first, the amphoteric radicles which give the Ostromisslenski and the xanthoproteic reactions are hydrolysed off, and then the hydrogen chondroitin sulphate. Using 1% of colloid, the chondrin is adsorbed as a whole, without decomposition. The optical rotation of some hydrogen chondroitin sulphate prepared in the above way is  $[\alpha]_D -46.59^\circ$ , whence  $[\alpha]_D$  for the chondrin residue is calculated to be  $-386.85^\circ$ .

R. T.

**Chondroitinsulphuric Acid.** W. SAVIALOV (*Z. physiol. Chem.*, 1923, 126, 219—249).—*Chondran*,  $C_{32}H_{36}O_{16}N$ , isolated as its tetrabenzoate,  $C_{66}H_{52}O_{20}N$ , is obtained from chondroitinsulphuric

acid on hydrolysis with acid, along with *chondroitine tribenzoate*, isolated as its *hydrochloride*,  $C_{40}H_{32}O_{12}N.HCl$ . This corresponds with a formula  $C_{19}H_{20}O_6N$  for chondroitine. Chondrosine,  $C_{19}H_{20}O_6N$ , has been isolated as the *osazone*,  $C_{26}H_{28}O_8N_6$ , light yellow, tufted crystals, m. p.  $154^\circ$  (corr.). The amorphous base,  $C_{19}H_{20}O_6N$ , has also been obtained, and the *sulphate*. Chondrosine, when heated with baryta water yields chitonic acid,  $C_{10}H_{10}O_6$ , and a base,  $C_7H_9N$  (*chloroplatinate*, white flocks,  $[C_7H_9N]_2.H_2PtCl_6$ ), and when oxidised, *isosaccharic acid*, m. p.  $208^\circ$ , is obtained. If chondrosine sulphate is warmed with an excess of copper hydroxide, compound,  $(C_5H_6O_4N)_2Cu$ , giving a red biuret reaction, is obtained.  
W. O. K.

**Keratin. IV. A. HEIDUSCHKA and E. KOMM** (*Z. physiol. Chem.*, 1923, 126, 261—276).—The proteoses obtained from the partial hydrolysis of horn (cf. A., 1922, i, 967) have been fractionated and the solubilities and reactions of the various heterokeratoses, protokeratoses, and deuterokeratoses investigated. W. O. K.

**The Preparation and the Properties of Ovokeratin. M. A. KUKULIN** (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 159—164).—A quantity of ovokeratin was prepared from the membranes of eggs, by Ladenburg's method. The sodium proteinate from the alkali washing of the membranes gave Adamkiewicz's, Molisch's, Pettenkofer's, and Ostromisslenski's reactions for albumins, and appears to be a hitherto unknown albuminate,  $[\alpha]_D -4.87^\circ$ . The subsequent etic acid washing removed from the membranes amino-acids, which gave only Ostromisslenski's reaction with picramic acid, and had  $[\alpha]_D -27.82^\circ$ . Ammonium and potassium ovokeratinate are prepared,  $[\alpha]_D$  being  $-36.79^\circ$ , and  $-38.96^\circ$ , respectively. Ovokeratin gives the biuret and the xanthoproteic reactions, and so Millon's and the above-mentioned four reactions. Its phosphorus content is very small, whilst 2.3% of sulphur is found. This is much lower than the value obtained by Lindval, who found 25% of sulphur in ovokeratin.  
R. T.

**Influence of Carnosine and of Different Ions on the Digestion of Proteins by Pepsin. IVAN ANDREEVITSCH SMORODINCEV** (*Russ. Physiol.*, 1922, 4, 279—280).—The activity of pepsin is not influenced by glycerol; extracts of the enzyme in this solvent maintain their activity for years.

The action of pepsin on edestin and casein is inhibited by the following substances in the concentrations (expressed as normality) stated: carnosine (1/160); sodium and potassium hydroxides (1/320—1/640); sodium, potassium, and lithium carbonates (1/160—1/320); sodium, potassium, and lithium hydrogen carbonates (1/20—1/40); ammonia (1/80); disodium hydrogen phosphate (1/8). The inhibitory effect is attributed to the hydroxyl-ions. No such action is shown by carnosine hydrochloride and nitrate (1/10), or by sodium, potassium, and ammonium chlorides and nitrates (1/10). The digestion of edestin by pepsin is inhibited by

1/4*N*-solutions of the chlorides and 1/8*N*-solutions of the nitrates of sodium, potassium, and ammonium, but that of casein is not influenced by normal solutions of these salts. The inhibitory action of salts is due to the anions.  
E. S.

**Adsorption of Saccharase by Alumina.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 127, 115—124).—The adsorption of saccharase by alumina is maximum at  $p_H$  6.0—6.5, using acetic acid and ammonium as a buffer, although with other buffers, particularly phosphates, irregular results are obtained. The addition of acetone to the solution of the enzyme increases the adsorption, but it also destroys the saccharase. Hence, only alcohol should be used to increase the adsorption of the enzyme.  
W. O. K.

**Inactivation of Saccharase by Halogens.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1923, 127, 99—114).—The degree of inactivation of saccharase by iodine increases with the time. In the case of bromine the degree is independent of the time. In both cases, it is independent of the concentration of the enzyme, and in the case of iodine, at least, it is independent of the  $p_H$ . Iodine appears to be more efficient than other poisons in inhibiting the activity of highly purified saccharase, whilst the bromine equivalent (the amount of saccharase inactivated by one molecule of bromine) agrees with that of silver as already determined.  
W. O. K.

**Existence of Two Amylotic Ferments in Malt Diastase.** E. OHLSSON (*Compt. rend. Soc. Biol.*, 1922, 87, 1183—1184; from *Physiol. Abstr.*, 1923, 8, 9).—In malt extract, two enzymes are present, one converting starch into dextrin, the other responsible for the conversion of starch or dextrin into maltose. These may be differentiated by keeping the enzymes at certain temperatures and at certain hydrogen-ion concentrations. At 5° and  $p_H$  4, the dextrin-forming enzyme disappears rapidly, whilst the maltose forming enzyme remains practically unaltered. Kept at  $p_H$  6 and at 70° for twenty minutes, the extract rapidly loses its property of forming maltose, while retaining its dextrin-forming capacity.  
W. O. K.

**Investigations on the Starch-liquefying Function of Malt Diastase.** W. WINDISCH, W. DIETRICH, and ARTUR BEYER (*Woch. Brau.*, 1923, 40, 49—50, 55—56, 61—63, 67—70).—The experimental results given indicate that the liquefaction of starch by diastase probably depends on increase in the degree of dispersion of the starch or amylopectin. The liquefying action proceeds best when  $p_H$  has the value 5.03, the reaction being the similar to the optimum reaction for saccharification of starch by diastase.

The method suggested for determining the liquefying power of malt diastase consists in treating amylopectin made from wheat starch with an aqueous extract of the malt in presence of a buffer mixture of sodium acetate and acetic acid, the filtered liquid being

afterwards hydrolysed by means of hydrochloric acid and the dextrose thus formed estimated iodometrically. The amount of starch liquefied by the diastase present in 1 g. of malt is taken as a measure of the liquefying power. Kjeldahl's law of proportionality is found to hold for the liquefying, as well as for the saccharifying, power, but the liquefying powers bear no constant relation to the saccharifying powers with different malts.

T. H. P.

**An Investigation of the Chemical Nature of Two Typical Enzymes: Pancreatic and Malt Amylases.** H. C. SHERMAN (*Proc. Nat. Acad. Sci.*, 1923, 9, 81—86).—A summary of work on enzyme hydrolysis (cf. A., 1922, i, 283). Preparations of pancreatic and malt amylases have been made, precautions being taken to reduce the hydrolysis of the enzyme. The pancreatic amylase showed marked enzymic activity at a dilution of 1:100,000,000, whereas the usual protein tests are 1,000 times less sensitive. Both the amylase preparations were submitted to quantitative analysis by the Van Slyke method, which showed that they yielded all the typical products of hydrolysis of proteins. The amylases were very much more sensitive to antiseptics which precipitate proteins than to those of the lipid dissolving type. The activity of the amylases decreases when suspended in pure water at a greater rate than when in the presence of substances which are the product of protein hydrolysis. The addition of amino-acids checks the deterioration of the enzyme as measured by the change in its saccharogenic power and amyloclastic activity. Arginine, histidine, lysine, tryptophan, and cystine were studied in this connexion. Arginine and cystine increase the activity of the amylases, but the other acids only exert a favourable influence on the saccharogenic power. The results show that the amyloclastic and saccharogenic activity are to some extent different properties of the amylase. The first products of the amylase are those amino-acids which tend to prevent the initial hydrolytic stages, and acids like lysine and tryptophan are produced in subsequent stages. This is in accord with the view that the amyloclastic occurs before the saccharogenic stage of enzyme action. The optimum activity of the two enzymes is shown at quite different hydrogen-ion concentrations, that of pancreatic amylase at  $p_H$  6.9 and of malt amylase at  $p_H$  4.4. The activity of the former is fully twice that of the latter.

W. E. G.

**Kinetics of Ester Hydrolysis by Liver Lipase.** E. KNAFFL-LENZ (*Arch. exp. Path. Pharm.*, 1923, 97, 242—261).—The hydrolysis of alkyl esters by the enzymes of the liver proceeds as a reaction of the first order, equal quantities being hydrolysed in equal times. The activity of the enzymes ceases at any  $p_H < 5.2$ , which is also the lowest  $p_H$  at which fats are hydrolysed. The optimum  $p_H$  for the hydrolysis of alkyl esters is 7.8—8.8, whilst in the case of fats, the optimum  $p_H$  is higher. In the hydrolysis of fats, if the reaction coefficient of the first order be calculated, it is found to decrease as the reaction proceeds.

W. O. K.

**Urease.** STURE LÖVGREN (*Biochem. Z.*, 1923, **137**, 206—257).—In continuation of the author's observations (A., 1922, i, 185) on urease, an investigation has been made of the influence on the position of the optimal  $p_H$ , of the phosphate concentration, the enzyme concentration, and the concentration of the reaction products. The empirical modification of the unimolecular equation given in the previous paper is not found to be generally applicable over the whole range of conditions studied. A new equation, developed from an equation of the type  $F(x, y, \dots, z) = \text{const.}$  is described containing five coefficients. For details of the evaluation of these constants the original should be consulted. H. K.

**Influence of Glycine on the Fermentative Action of a Soja-bean Urease.** NAOSABURO KATÔ (*Biochem. Z.*, 1923, **136**, 498—529).—A long series of experiments is detailed on the influence of glycine on the action of urease. The salient points are the following. Using a single urease preparation, for a given quantity of urease, there is an optimal carbamide concentration which is termed the "equivalent carbamide concentration" (*E.C.C.*) which is uninfluenced by dilution or temperature changes. It follows that the ratio of the ammonia formed at a given carbamide concentration to that formed at the equivalent carbamide concentration is a variable quantity and is called the "gradation" of the urease action for this particular carbamide concentration. The gradation is subject to temperature influences and such changes are called the "quality" of the gradation. The magnitude of the *E.C.C.* increases with increase of the quantity of urease used. The quantity of ammonia evolved at the *E.C.C.* is a constant for the urease preparation. Addition of glycine influences these three "constants" in such a way that more ammonia is evolved. If the experiment is repeated with more glycine, then the proportion of ammonia below the *E.C.C.* is unchanged, but above the *E.C.C.* there is more evolved than in the former experiment. In urease preparations, two constituents are postulated to account for the great variations possible in the experimental results. H. K.

**Analogies between Methylene-blue and Oxydases.** P. A. ASCHMARIN (*J. Russ. Physiol.*, 1922, **4**, 283—284).—Methylene-blue accelerates considerably the indophenol and *p*-phenylenediamine reactions. In the former case, the velocity is augmented five to ten times, and in the latter five to twenty times, according to the concentrations of the reagents and the temperature. The last-named factors exert a similar influence in the presence of methylene-blue as in the presence of oxydases (cf. Vernon, A., 1911, ii, 750; Battelli and Stern, A., 1913, i, 139, 140). Methylene-blue may be considered as a substance analogous to the oxydases. E. S.

**The Interaction of Hydrogen Sulphide, Thiocyanogen, and Thiocyanic Acid with Unsaturated Compounds.** FREDERICK CHALLENGER, ALAN LAWRENCE SMITH, and FREDERIC JAMES PATON (*T.*, 1923, **123**, 1046—1055).

Organo-derivatives of Thallium. VI. Compounds of the type  $R_3TlX$ . ARCHIBALD EDWIN GODDARD (T., 1923, 123, [61—1172]).

### Physiological Chemistry.

**The Immediate Effect of Heavy Exercise (Stair-running) in some Phases of Circulation and Respiration in Normal Individuals. II. Oxygen and Carbon Dioxide Content of Blood Drawn from a Cubital Vein at Different Intervals after Exercise.** CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1923, 55, 477—485).—The oxygen content of blood from the cubital vein, which has a low value immediately after heavy leg exercise (this vol., i, 502), increases to a value almost equal to that of arterial blood in two to four minutes and returns to the normal in five to eight minutes after the cessation of such exercise. Simultaneously with the increase in oxygen content, the carbon dioxide content decreases markedly (5 to 10 vol. %); this is probably due to accumulation of lactic acid in the muscles.

E. S.

**Physiology of Muscular Exercise. I. Changes in Acid-base Equilibrium following Short Periods of Vigorous Muscular Exercise.** DAVID P. BARR, HAROLD E. HIMWICH, and ROBERT P. GREEN (*J. Biol. Chem.*, 1923, 55, 495—523).—Short periods of vigorous leg exercise are followed by a large diminution in the carbon dioxide capacity, a reduction in the alkalinity, and an increase in the lactic acid content of both arterial and venous blood (drawn from the arm). In the case of arterial blood, there is also a diminution in the carbon dioxide tension; venous blood as not yielded consistent results in this respect. No quantitative relationship has been observed between the reduction in carbon dioxide capacity and the increased concentration of lactic acid. The above changes vary in magnitude according to the vigour of the work; they are scarcely detectable after light exercise.

E. S.

**Physiology of Muscular Exercise. II. Comparison of Arterial and Venous Blood following Vigorous Exercise.** DAVID P. BARR and HAROLD E. HIMWICH (*J. Biol. Chem.*, 1923, 55, 525—537).—The diminution in the carbon dioxide capacity of blood drawn from the arm shortly after vigorous leg exercise (cf. preceding abstract) is smaller in venous than in arterial blood. This is due to the removal of lactic acid from the blood during its circulation through the tissues of the arm. In the region of the active tissues, however, the venous capacity is equal to, or less than, the arterial. Apparently, lactic acid passes from the active muscles into the blood, from which it is again removed by

the less active tissues. There is no appreciable difference between the reaction of arterial and of venous blood following exercise.

E. S.

**Physiology of Muscular Exercise. III. Development and Duration of Changes in Acid-Base Equilibrium.** DAVID P. BARR and HAROLD E. HIMWICH (*J. Biol. Chem.*, 1923, 55, 539-555).—The carbon dioxide tension of arterial blood increases during the first two minutes of vigorous exercise and thereafter diminishes progressively; the return to the normal takes place slowly and commences several minutes after exercise has ceased. With venous blood, the increase continues during a longer period. The remaining changes in the blood (cf. preceding abstracts) are continuous from the commencement of exercise, reach a maximum either during exercise, if this is continued for about seven and a half minutes, or after exercise, if it is of shorter duration; the return to the normal then takes place slowly. The direction of the changes at any particular time is apparently conditioned by the difference in the rates at which lactic acid is being absorbed by, and removed from, the blood.

E. S.

**Seasonal Tide of Blood Phosphates in Infants.** A. F. HESS and M. A. LUNDAGEN (*J. Amer. Med. Assoc.*, 1922, 79, 2210-2212).—The seasonal tide of blood phosphates with a diet of raw milk showed a decline from about 4 mg. % in December to 3½ mg. % in March, after which the blood phosphates quite steadily rose to 4.5 mg. % in June. The low level of phosphates in March would have been lower but for the fact that whenever the phosphates fell to 3.75 mg. % the child was given either sun treatment or irradiation from an artificial source. Ultra-violet light can also raise to normal a subnormal amount of calcium in the blood. In some experiments, 7 mg. % have been raised to 10 by irradiations during two or three weeks with the carbon arc light. The seasonal variation indicates that the chemical constitution of human blood is not constant for all periods of the year. This probably is true for other tissues. Marked fluctuations are observed only in young children. Seasonal changes in the composition of the blood appear to be correlated with certain seasonal diseases.

CHEMICAL ABSTRACTS.

**Blood Lipids. I. The Relation of Cholesterol and Protein Deficiency to Basal Metabolism.** A. A. EPSTEIN and HERMAN LANDE (*Arch. Intern. Med.*, 1922, 30, 563-577).—A low blood cholesterol value was found associated with high basal metabolism and a high blood cholesterol value with a low basal metabolism. Thus, a low blood cholesterol value was observed in hyperthyroidism and a low basal metabolism in nephrosis.

CHEMICAL ABSTRACTS.

**Variation in the Lipoid Content of the Plasma after Injection of Peptone. Comparison with Anaphylactic Shock.** (MME) PAULETTE JUNG and RENÉ WOLFF (*Bull. Soc. Chim. biol.*, 1923, 5, 200-206).—Intravenous injection of Witte's peptone into

Dogs produced large variations in the lipid content of the plasma. The fatty acid content increased consistently, the increase in one case amounting to 87% (calculated on the dry weight of the plasma); the variations in cholesterol and lipid phosphorus were, however, irregular. Values approaching the normal were again obtained when the coagulability of the plasma returned. Preliminary experiments indicate that there is also a disturbance in the lipid content of the plasma during anaphylactic shock. E. S.

**Is Pyruvic Acid the Forerunner of Acetaldehyde in Human Blood? The Presence of Carboxylase in Human Blood.**

WILHELM STEPP and BEHREND BEHRENS (*Z. physiol. Chem.*, 1923, 127, 80—92).—By the use of the "silver" method of Stepp and Fricke (*A.*, 1922, ii, 236) for the estimation of acetaldehyde, estimations have been made of the amount produced from pyruvic acid in the presence of blood. It is concluded that a carboxylase is present in small quantities in the blood. W. O. K.

**Comparative Concentration of Urea in the Blood and Saliva in a Series of Pathological Cases.** H. W. SCHMITZ (*J. Lab. Clin. Med.*, 1922, 8, 78—82).—The urea content of saliva was about 89.4% of that of the blood; salivary urea estimations may replace those of blood urea in determinations of the functional activity of the kidneys. CHEMICAL ABSTRACTS.

**Decomposition of Glycogen by Blood-serum.** DIONYS FUCHS and GEZA HETÉNYI (*Biochem. Z.*, 1923, 135, 469—470).—The change of rotation of the blood-serum of diabetics and of non-diabetics when mixed with 1% glycogen solution was observed in eighty cases. In thirty-three cases the total mean change of rotation in diabetics was  $-0.053^\circ$ , in non-diabetics  $-0.036^\circ$ , and in forty-seven cases (different observer) for diabetics  $-0.070^\circ$ , and for non-diabetics  $-0.063^\circ$ . The conclusion is drawn that the diabetic blood-serum has a greater power of breaking down glycogen than that of the non-diabetic. H. K.

**Nature of Antiferments (Antitrypsin).** BORIS I. SLOVITZOV and W. JA. XENOPHONTOVA (*J. Russ. Physiol.*, 1919, 2, 267).—Evidence is advanced supporting Jobling's view that antitrypsin is a lipid. Thus, serum, when extracted with chloroform, loses its antitryptic power, whilst the soap obtained by saponification of the extract has the same antitryptic power as the serum. Sodium oleate in minimal concentrations (0.003%) has also been observed to exert a marked antitryptic action. Glycerol does not show this effect. E. S.

**Digestion. I. The Digestive Enzymes of Coelenterates.**  
**II. Digestion in Elasmobranchs and Teleosts.** M. BODANSKY and W. C. ROSE (*Amer. J. Physiol.*, 1922, 62, 473—481; 482—487).  
 I. The following enzymes are present in the jelly fish, *Stomolophus metagris*, and in the Portuguese man-of-war, *Physalia physalis*: pepsin, trypsin, rennin, amylase, maltase, and lipase. Invertase is present in negligible amount. Inulinase and lactase are absent. z\* 2 •

Proteins naturally used as food (fish) are more readily hydrolysed than are proteins foreign to the customary diet (egg-albumin, beef fibrin and casein), suggesting a specific adaptation of the enzymes to the individual proteins on which they customarily act.

II. A peptic enzyme, having a maximum activity at a  $p_H$  of about 3.0, was demonstrated in the gastric mucosa of the elasmobranchs *Squalus acanthias* (dogfish), *Pristis pectinatus* (sawfish), *Torpedo galvani* (torpedo ray) and in the teleosts *Lutjanus aya* (red snapper), *Paralichthys lethostigma* (flounder), *Lactophrys tricornis* (cowfish) and *Mycteroperca bonaci* (black grouper). Fish pepsin effectively digests a larger variety of proteins than does the pepsin of either jellyfish or of Portuguese man-of-war. Rennin is present in the stomach of the torpedo ray, red snapper, flounder, and catfish; but absent from that of the dogfish, sawfish, cowfish, and mullet. The pyloric caeca of the red snapper contain trypsin, pepsin, rennin, amylase, and lipase; inulinase, maltase, and lactase are absent. The secretions of the pyloric appendages of the red snapper contain most of the enzymes which are usually found in the pancreatic juice of higher vertebrates.

CHEMICAL ABSTRACTS.

**The Structure of the Alimentary Canal and its Enzymes in the Bee (*Apis mellifera*, L.).** E. N. PAVLOVSKI and E. J. ZARIN (*Quart. J. Microsc. Sci.*, 1922, 66, 509—556).—The stomach (mid intestine) of the worker and drone contained catalase, amylase, invertase, lipase, pepsin, trypsin, and rennin. Inulase, lactase, and emulsin were absent. Catalase was found in the rectum, but was subject to seasonal variation. From triturated stomachs, catalase decreased in the extracts on keeping, whilst from whole stomachs it increased. Glycerol had a repressive influence on invertase. Methods for the preparation of extracts and for testing their activity are given.

CHEMICAL ABSTRACTS.

### Uric Acid Metabolism. III. The Influence of Fats and Carbohydrates on the Endogenous Uric Acid Elimination.

HOWARD B. LEWIS and RALPH C. CORLEY (*J. Biol. Chem.*, 1922, 55, 373—384).—The experimental conditions were similar to those employed in the case of proteins and protein derivatives (A., 1918, i, 277). No increased excretion of uric acid was observed after the ingestion of cream (135 g.), lactose (100 g.), sucrose (100 g.), or dextrose (100 g.). Increases were, however, produced by glycerol (50 g.), honey (200 g.), and commercial glucose syrup (200 g.), the effect being most marked in the case of glycerol. When these and the previous results are regarded from a quantitative point of view, the stimulating action of the substances on uric acid excretion is found to run roughly parallel with the specific dynamic action. It is considered that these results are in harmony with the view previously advanced that a rise in uric acid excretion following the ingestion of food is due, at least in part, to a stimulation of cellular metabolism.

E. S.

**Histochemistry of Spermatogenesis.** H. STEUDEL and K. SUZUKI (*Z. physiol. Chem.*, 1923, 127, 1—13).—Fish testicles were

shaken with water, filtered, and the filtrate evaporated to a syrup. When kept, a sediment separated, which consisted of inorganic salts and gave reactions for tryptophan, creatinine, and cystine, and from which leucine was isolated. In the filtrate from the deposit, the presence of alanine, leucine, lysine, creatinine, agmatine, and histamine was determined.

W. O. K.

**Some Physico-chemical Properties of the Constituents of the Egg of *Paracentrotus lividus*, Lk.** FRED VLÈS, (Mlle) G. ACHARD, and DJ. PRIKELMAIER (*Compt. rend.*, 1923, **176**, 1179—1181).—Portions of the unfertilised eggs of *Paracentrotus lividus* were made into an emulsion with acidified sea-water having  $p_H$  5·8 equal to that of the interior, and the emulsion was subjected to cataphoresis in sea-water of  $p_H$  3, 4·1, 5·0, 5·8, and 9. A distinct transport to the cathode was observed in  $p_H$  3, 4·1, and 5·0, and to the anode in  $p_H$  9. In  $p_H$  5·8, the direction was uncertain, but with a slight tendency towards the anode. The isoelectric point of one of the principal constituents of the ovular complex corresponds therefore with a  $p_H$  between 5·0 and 5·8. Experiments with an emulsion of  $p_H$  8 gave less regular results, and it appears that the complex shows a maximum coherence in the neighbourhood of the isoelectric point, and any variation in the  $p_H$  of the interior of the egg produces a corresponding change in the viscosity, conductivity, osmotic pressure, etc., and will explain the observations previously made on the effect of change of  $p_H$  on fecundation, division of the egg, etc.

G. F. M.

**Distribution of Nitrogen between the Body of the Mature Chick, the Yellow of the Egg, and the Waste [Shell, Amnion].** N. W. ROMENSKI (*J. Russ. Physiol.*, 1919, **2**, 284).—The body of the new-born chick contains 54·12—65·82%, the yellow of the egg 27·63—37·01%, and the waste 6·42—12·68% of the total nitrogen of the egg. If the chick is left without food for thirty-six hours after birth, there is practically no diminution in the nitrogen it contains.

E. S.

**Chemical Composition of the Grey Substance of the Human Brain in Relation to the Function of the Brain.** A. K. LENZ (*J. Russ. Physiol.*, 1919, **2**, 168—169).—The essential differences between the composition of the grey matter of the cortex and that of the ganglia are a greater proportion of water and proteins in the former and of lipoids in the latter. The proteins in the two portions are of similar type. These results indicate the important rôle of the proteins in the function of the brain.

E. S.

**Chemical Composition of the Grey and White Matter of the Human Brain.** B. I. SLOVTOV and A. M. GEORGIEVSKAIA (*J. Russ. Physiol.*, 1922, **4**, 277).—Analyses have been made of the grey and white matter of the brain. The former is richer in proteins and extractives, and the latter in lipoids. The composition of rabbit's brain is distinctly modified, especially in the lipid fraction, by methyl-alcoholic poisoning.

E. S.

**Autolysis of the Grey Matter of the Brain.** A. M. GEORGIEVSKAIA (*J. Russ. Physiol.*, 1922, 4, 277).—During autolysis of the brain both the proteins and lipoids dissolve. After some time, however, the insoluble fractions of these substances may increase owing to the formation of less soluble products. There is a considerable increase in amino-nitrogen during autolysis of the brain.

E. S.

**The Nucleic Acids of the Pancreas.** H. STEUDEL and SATOSU NAKAGAWA (*Z. physiol. Chem.*, 1923, 126, 250—256).—In the pancreas, guanine and adenine are present in equimolecular proportions. Apparently about 5 g. of nucleic acid are contained in 100 g. of the dry residue, obtained after extraction of the glands by alcohol and ether.

W. O. K.

**Pancreatic Rennin.** A. EPSTEIN (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 3—6).—By suitable treatment (detailed in the original communication) of pancreatic extract, a substance which conceals the presence of rennin can be removed. Rennin is so far inseparable from trypsin, and combined they constitute about 1—2% of dry pancreatic extract as an acidic substance of protein nature, hygroscopic, coagulating at 82—85°, not removed by ordinary precipitants, and active only in the presence of calcium-ions.

CHEMICAL ABSTRACTS.

**The Effect of Pancreatic Rennin on Blood Coagulation.** A. EPSTEIN and NATHAN ROSENTHAL (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 79—84).—Pancreatic rennin-trypsin (cf. preceding abstract) together with calcium chloride reduce the coagulation time of normal blood from 11—12 minutes to 0.25—0.5 minute. The coagulation time varies inversely with the amount of enzyme.

CHEMICAL ABSTRACTS.

**The Question of the Cadaverine Content in Aqueous Extracts of Autolysed Pancreatic Glands.** (MLLE) V. A. SEMENOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 608—612).—A sterile extract made from 12 kilos. of pancreatic glands derived from freshly killed cattle was tested for the presence of cadaverine (pentamethylenediamine), using Werigo's method (A., 1892, 1368). The mixed picrates of the bases present proved to contain a compound having the melting point of arginine picrate, but no cadaverine could be found (cf. Kutscher and Lohmann, A., 1904, ii, 425; 1905, ii, 466).

G. A. R. K.

**Nervous Control of the Kidney in Relation to Diuresis and Urinary Secretion. VI. The Effect of Unilateral Section of the Splanchnic Nerve on the Elimination of certain Substances by the Kidney.** E. K. MARSHALL, jun., and M. M. CRANE (*Amer. J. Physiol.*, 1922, 62, 330—340).—Increased blood flow through the kidney, brought about by section of the splanchnic nerve, increases markedly the elimination of water, chlorides, and carbonates, to a less extent that of urea, phosphates, and sulphates, whilst the elimination of creatinine, ammonia, and phenol-

phosphophthalein is unchanged. The results are thought to support the theory of filtration through the glomeruli and reabsorption and secretion by the tubules.

## CHEMICAL ABSTRACTS.

**Hippuric Acid Synthesis as a Test of Renal Function.**

ERIGIUS MORGULIS, G. P. PRATT, and H. M. JAHR (*Arch. Intern. Med.*, 1923, **31**, 116—144).—In normal persons, 2 g. of benzoic acid, administered as such or as the sodium salt, is completely synthesised to hippuric acid and the kidney is stimulated to enhanced activity. In nephritic and cardiorenal patients the synthesis is never complete but, even in severe nephritis, from 53 to 95% of the ingested benzoic acid may be recovered as hippuric acid and from 59 to 100% as total benzoic acid in the twenty-four hours following the administration of benzoic acid.

## CHEMICAL ABSTRACTS.

**Relation of Lipoids to Suprarenal Physiology. I. The Cholesterol and Lipoid Phosphorus Contents of the Blood of Rabbits Before and After Suprarenalectomy.** EMIL J. LAUMANN and O. M. HOLLY (*J. Biol. Chem.*, 1923, **55**, 457—475).—

A rise in the blood lipid phosphorus was observed in every case after removal of both glands and occasionally after removal of one, but no significant changes occurred in the cholesterol content. During the few days preceding the death of the animals, both the cholesterol and the lipid phosphorus content of the blood rose; these changes, however, were probably due to blood concentration. The results thus offer no support for the hypothesis that cholesterol is either formed or stored in the suprarenal glands.

E. S.

**The Active Principles of the Pituitary Gland.** HAROLD VARD DUDLEY (*J. Pharm. Expt. Ther.*, 1923, **21**, 103—122).—

Further unsuccessful attempts have been made to isolate the uterine stimulant from extracts of powdered pituitary glands. The greater part of the active principle was found to be concentrated in the alcohol-soluble portion of the butyl alcohol extract previously described (*A.*, 1920, i, 344). From this, creatinine was isolated in the form of its double picrate with potassium. The mother-liquors from the crystallisation of this salt gave a preparation of high activity, which was further separated into two fractions by means of acetone. The insoluble fraction consisted of a dry powder with an activity on the isolated uterus about twelve times as great as that of histamine; when tested on the blood pressure, it gave a pure pressor effect. The soluble fraction was a deliquescent mass with a much smaller uterine activity; its pressor action was preceded by a depressor effect. The author concludes, in opposition to the view of Abel and Rouiller (*J. Pharm. Expt. Ther.*, 1922, **20**, 1), that at least three active principles are present in pituitary extracts.

E. S.

**Substances Extractable from Human Muscle.** I. A. MORODINCEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 263—266).—

The extract was made of fresh human muscle, and was analysed for bases in the usual way. The muscle thus extracted contained

0.45% of nitrogen, and the following bases were isolated: Purine bases, 0.036%, carnosine, 0.164%, methylguanidine, 0.041%, carnitine, 0.031%, creatinine, traces. The same substances exist in similar proportions in the muscles of domestic animals.

R. T.

**Creatinine and Creatine in Muscle Extracts. IV. Concerning the Formation of Creatine from Methylguanidine in Muscle.** FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1923, 55, 323).—Incubation of extracts of muscle tissue with methylguanidine under various conditions led to no increase in total creatine. This supports the results of Baumann and Hines (*A.*, 1918, i, 417) and is against the view that methylguanidine is the precursor of creatine.

E. S.

**The Rate of Deposition and Paths of Absorption of Strontium in the Rat.** ETHEL MAY KINNEY and E. V. MCCOLLUM (*J. Pharm. Expt. Ther.*, 1923, 21, 165–176).—When fed to rats in the form of carbonate, strontium is rapidly deposited in the bones, even although adequate amounts of calcium are present in the diet. The rate of deposition is greater with young than with mature animals. Strontium may also enter the body through the placenta and the milk of the mother.

E. S.

**The Zinc Content of the Body and certain Organs of Invertebrates.** GABRIEL BERTRAND and R. VLADESCO (*Bull. Soc. chim.*, 1923, [iv], 33, 341–345).—The zinc content of the whole bodies, and also of certain specific organs of numerous molluscs, was determined by the method previously described (*ibid.*, 1921, 29, 53), and quite exceptionally large amounts were found in oysters (*Ostrea edulis*), ranging up to 27 mg. per 100 g. of the fresh material, and 152 mg. per 100 g. of dry material. Still larger quantities of from 50–131 mg. per 100 g. of fresh material were found in Portuguese oysters (*Gryphea angulata*). The average content of other shell fish such as mussels, cockles, etc., was 2–5 mg. per 100 g. The distribution of the zinc in the various organs was very uneven, being in general lowest in the muscular portions. The metal appears to play an important part in the phenomenon of fecundation.

G. F. M.

**Growth of Caterpillars.** EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 127, 93–98).—Determinations have been made of the weight and of the nitrogen content of caterpillars at various periods in their development.

W. O. K.

**The Transformation of Proteins.** P. A. GLAGOLEV and M. N. VISCHNIKOV (*J. Russ. Physiol.*, 1917, 1, 25).—No appreciable difference has been observed in the composition of silk obtained from silkworms fed on the leaves of *Maclura aurantiaca* and on mulberry leaves (*Morus var. Tatarica*). The percentages of sericin and of fibroin, and the amino-acid composition of the latter, were practically identical in the silk from the two sources. The cocoons from the worms on the first diet, however, had a larger fat content.

E. S.

**The Effect of Heat on the Calcium Salts and Rennin Coagulability of Cow's Milk.** L. S. PALMER (*Proc. Soc. Exp. Biol. Med.*, 1921, **19**, 137—142).—The fact that a colloidal suspension of calcium hydrogen phosphate is largely precipitated by heating at 63° for thirty minutes explains the loss of the salt when milk is pasteurised. Dialysed milk is not coagulated by rennin in several hours, but the further addition of a small quantity of calcium chloride or hydrogen chloride causes instant clotting. Experiments show that a solution of colloidal calcium hydrogen phosphate and gelatin does not affect coagulation by rennin.

CHEMICAL ABSTRACTS.

**The Presence of Formic Acid in the Urine of Infants and Older Children.** M. McNEAL and CH. J. ELDRIDGE (*Amer. J. Diseases Children*, 1922, **23**, 419—422).—Examination of the urine of children by a modification of Autenrieth's method demonstrates the presence of formic acid.

CHEMICAL ABSTRACTS.

**Ingested Fat and Body Fat as Precursors of the Acetone Substances.** ROGER S. HUBBARD (*J. Biol. Chem.*, 1923, **55**, 357—363).—On diets moderately low in antiketogenic material, the amounts of acetone compounds excreted are the same whether they are derived from ingested or from tissue fat.

E. S.

**The Relation between Creatine Excretion and Acidosis.** ALEXANDER PALLADIN (*Biochem. Z.*, 1923, **136**, 359—365).—The total nitrogen, creatinine, creatine, and acetone content of the urine of fasting dogs which received a daily injection of phloridzin was followed daily. Regarding the acetone substances in the urine as a measure of the acidosis, it is found that creatine excretion is apparently independent of the acidosis. Such dogs given small quantities of protein show diminished acetone products but unchanged creatine excretion. Fats increase the acetoneuria without influencing the creatine excretion. The acidic or basic character of the foodstuffs is likewise without influence on the creatine.

H. K.

**Influence of Cooling on the Excretion of Creatine.** ALEXANDER PALLADIN (*Biochem. Z.*, 1923, **136**, 353—358).—Rabbits cooled until the rectal temperature fell to 30° excrete creatine in the urine as well as dextrose. If, however, the diet contains copious carbohydrate, no creatine appears.

H. K.

**Secretion of Bile Acids in Cystinuria.** HANS EPPINGER (*Arch. expt. Path. Pharm.*, 1923, **97**, 51—53).—An analysis has been made of the contents of the gall-bladder in a case of cystinuria. Sodium taurocholate appears to be decreased, as compared with the normal.

W. O. K.

**The Natural Porphyrins.** O. SCHUMM (*Z. physiol. Chem.*, 1923, **126**, 169—202).—The porphyrin in the urine of normal and of diseased subjects, and more particularly in cases of lead poisoning, has been investigated. The blood in some cases of congenital æmatoporphyrinuria has been examined and the serum found to

contain porphyrin and hæmatin, besides a small quantity of oxyhæmoglobin and sometimes much bilirubin. W. O. K.

**Theory of Narcosis by Inhalation Anæsthetics. II. Narcosis by Indifferent Gases under Pressure.** KURT H. MEYER and HEINR. HOPFF (*Z. physiol. Chem.*, 1923, 126, 281—298).—It is found that with indifferent gaseous or volatile substances of very different types, narcosis sets in when the pressure of the vapour is such that the concentration of the substance in the cell lipoid has reached a certain approximately constant value, 0.05–0.18 mol. per litre, according to the type of animal employed.

W. O. K.

**Production of Muconic Acid from Benzene in the Animal Organism.** HANNS NEUMAERKER (*Z. physiol. Chem.*, 1923, 126, 203—209).—If muconic acid be injected subcutaneously into a rabbit, about 60% may be recovered from the urine. On the other hand, after the injection of benzene in quantities of 1–3 g., no muconic acid could be detected in the urine. This indicates that if muconic acid is formed from benzene in the body, the amount produced is small.

W. O. K.

**Synthesis of Amino-acids in the Animal Organism. II. The Synthesis of Ornithine in the Body of the Fowl.** JAMES H. CROWDLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1923, 55, 365—371).—When fed to fowls on a nitrogen-free diet, benzoic acid was excreted partly unchanged and partly as ornithuric acid. Simultaneously, there was a slight increase in the amount of uric acid excreted, but the percentage, calculated on the total nitrogen eliminated, showed a considerable decrease. Apparently, ornithine can be synthesised from waste uric acid nitrogen. No increased production of ornithuric acid was observed when histidine and proline were fed simultaneously with the benzoic acid; arginine, however, produced this effect.

E. S.

**The Pharmacological Effect of the Three Stereoisomerides of Camphor, and of some Camphor Derivatives, on Smooth Muscle.** MAX DOHRN (*Arch. expt. Path. Pharm.*, 1923, 97, 38—50).—*l*-Camphor has a greater paralysing effect on smooth muscle than the racemic form, and this again a greater effect than *d*-camphor. Other camphor derivatives, including *i*-aminocamphor, dihydrocamphenepyzazine, dihydrocamphenepiperazine, camphorquinone, methylidicamphorylcarbinol, oxymethylenecamphor, camphorylcarbamide, camphoryl- $\psi$ -carbamide, camphoryl- $\psi$ -semi-carbazide, and dicamphorylcarbamide have also been investigated as to their pharmacological effects.

W. O. K.

## Chemistry of Vegetable Physiology and Agriculture.

## Formation of Fats and Lipoids. I. Influence of the Nature of the Carbohydrate Food on the Fat Content of the Tubercle Bacillus, and the Characters of these Fats.

EMILE F. TERROINE and J. E. LOBSTEIN (*Bull. Soc. Chim. biol.*, 1923, 5, 182—199).—The influence of the composition of the culture medium on the lipid content of the tubercle bacillus has been investigated. With a medium otherwise identical, but containing dextrose in place of glycerol, the fat content of the bacilli diminished by about 60%; at the same time there was an increase in the protein content. The tubercle bacillus contains minimal quantities of cholesterol.

E. S.

## The Effect of Reaction on the Fixation of Nitrogen by Azotobacter.

H. W. JOHNSON and C. B. LIFMAN (*Univ. California Pub. Agr. Sci.*, 1922, 4, 397—405).—A vigorous strain of *Azotobacter croococcum* was grown in solutions of which the reactions were definitely determined by the hydrogen electrode. The nitrogen fixed in the solution of each reaction was estimated and the changes in reaction during incubation were measured. The reaction of the solution below  $p_H$  8.0 changed very little, because below  $p_H$  8.0 no growth occurred, and between 6.0 and 8.0 the solution was highly buffered. Above  $p_H$  8.0, the reaction changed greatly, possibly because of incomplete reaction of the alkali at the time of saturation, but more probably because of absorption of carbon dioxide by the strong alkali. The amount of nitrogen fixed was not greatly affected by reactions between  $p_H$  values of 6.2 and 8.8, although reactions around  $p_H$  7.0 and 8.0 seemed to be most favourable. Slight changes outside of these values caused an abrupt decrease in fixation.

CHEMICAL ABSTRACTS.

## The Coagulative Enzyme of the Yeast-cell.

A. M. NASTUKOV and N. S. PIATNICKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 183—186).—An enzyme extracted from macerated yeast-cells is found to retain its power of coagulating so-called nutritive yolk-of-egg solution after heating in an autoclave at a pressure of 1.25 atmospheres. The product of coagulation, after filtering and extracting with alcohol, ether, or chloroform, gave on analysis, C 48.06%, H 7.06%, N 11.53%, S 0.98%, and P 5.46%. This shows that it cannot be vitellin or  $\psi$ -nuclein, formed by the action of pepsin, or of endotryptase, contained in yeast-cells, on yolk of egg. Yeast cells, therefore, must contain two enzymes, endotryptase, and a coagulative enzyme.

R. T.

## The Fermentation of Glyceric and Pyruvic Acids.

A. N. LEBEDEV and A. N. POLONSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 93—94).—A short résumé of the work on the subject. Both acids are fermented by yeast to carbon dioxide and acetaldehyde, but whilst sugar solutions are completely fermented under com-

parable conditions, pyruvic acid gives only a 40% yield of decomposition products (other than carbon dioxide); the yield from glyceric acid is somewhat more favourable.

It is suggested that the experimental facts do not support the view that pyruvic acid is an intermediate compound in the alcoholic fermentation of sugar and that glyceric acid could equally well be such an intermediate product.

G. A. R. K.

#### The Fermentation of Pyruvic Acid in the Presence of Sugar.

A. N. LEBEDEV and A. N. POLONSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 328—344).—Solutions containing pyruvic acid and sucrose in various proportions were fermented by yeast. The quantity of carbon dioxide produced from such mixtures is greater than when each alone is fermented, whilst the yields of alcohol and acetaldehyde are diminished. This is probably due to the differential actions of zymase and carboxylase. Curves are drawn showing the velocities of fermentation of sucrose and pyruvic acid, separately and together, and at various concentrations. These show that fermentation proceeds more slowly in the mixture than for the separate components. If the solution be neutralised or made alkaline, the yields of acetaldehyde diminish, showing that carboxylase is less active in such conditions. Both the latter enzyme and zymase at first act rapidly and then very slowly, contrary to the views of Palladin, Gromov, and Monteverde (*A.*, 1914, i, 604). Less acetaldehyde is reduced to alcohol as the proportion of sugar in the mixture increases.

R. T.

**The Fermentation of Glyceric and Pyruvic Acids.** A. N. LEBEDEV and A. N. POLONSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 344—357).—Glyceric acid was fermented by yeast, and the quantity of carbon dioxide, acetaldehyde, and acetic acid produced were measured. The values thus obtained show that the reaction cannot consist only of the elimination of carbon dioxide from the acid, but may also involve more complete oxidation. Similar measurements were made for pyruvic acid, in acid, neutral, and weakly alkaline solutions. The amount of carbon dioxide produced is greatest with acid solutions, whilst with neutral or alkaline solutions the amount produced corresponds with the reaction  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2 + \text{CH}_3\cdot\text{CHO}$ . The acetaldehyde thus produced is converted partly into alcohol and acetic acid by the Cannizzaro reaction, and partly into alcohol by reduction, 2.5 times as much of the latter being formed as of the acid. More carbon dioxide and alcohol are produced from pyruvic than from glyceric acid, and less acetaldehyde and acetic acid. Not more than 40% of pyruvic acid is used in the production of the latter two substances and of alcohol, showing that it cannot be an intermediate product in the formation of alcohol by the fermentation of sugars.

R. T.

**Action of Ultra-violet Rays on Alcoholic Fermentation by *Botrytis cinerea*.** ROMOLO DE FAZI (*Atti R. Accad. Lincei*, 1923, [v], 32, 235—236).—Fermentation of must from grapes infected with *Botrytis cinerea* is accelerated by exposure of the must to the light from a quartz mercury vapour lamp.

T. H. P.

**Iron and Manganese Content of certain Species of Seeds.** S. MCHARGUE (*J. Agric. Res.*, 1923, 23, 395—399).—Analysis of a large number of seeds showed that in grasses and cereals the manganese content was roughly equal to that of iron; but in leguminous plants the amount of iron was considerably greater than that of manganese. A. G. P.

**Influence of Potassium on the Development of Plants and on their Morphological and Anatomical Structure (with Special Consideration of Farm Crops).** H. WEISZMANN (*Z. Pflanzenphysiologie*, 1923, 2, 1—79).—A large number of pot and sand culture experiments are described in which the effects of potash starvation, and of fertilisation at different periods of the plant's growth, on the development of individual plant organs is studied. Unlike nitrogen- and phosphate-starvation, a deficiency of potassium does not markedly affect the plant structure in the early stages, but the wilting and death of the plant soon occurs. The plant loses its power of synthesis (particularly in the case of sugar beet) and the reserve storing organs (fruits, seeds, tubers, etc.) show retarded development at all. The latter effects are those most noticeably remedied when potassium is afterwards supplied to the starved plant.

Potassium affects the development of individual organs only in so far as its total-yield increasing action proceeds. Flowering and fruiting are increased by potassium feeding, but to a lesser extent than in the case of phosphates. With cereals, potassium manuring increases the weight and size of individual grains, but does not often increase the actual number of grains, as does phosphatic manuring. Potassium increases the size and quantity of potato tubers, and the size of root crops. The enlarged top growth (stems and leaves) produced by supplying potassium to a previously starved plot results mainly from longer leaves and stems and not from a greater number of them. Deficiency of potassium frequently causes deformity in leaves, notably curling and spotting, and may also affect the colouring of leaf, stem, and grain. The mechanical properties of cereal straws are improved by potassium manuring; with non-cereals, the length of side shoots and their terminal spacing is increased, but the actual number of shoots is but little altered. The action of potassium on plants in general is not so uniform as that of nitrogen and phosphates. Consistent effects of potassium on the anatomical structure of plants can only be traced in a few instances, and then only with difficulty.

A. G. P.

**A New Method for the Separate Extraction of Vacuole and Cytoplasmic Material from Leaf-cells.** ALBERT CHARLES EMBALL (*J. Biol. Chem.*, 1923, 55, 333—342).—The method depends on the fact that, after plasmolysis by immersion in an organic solvent such as ether or butyl alcohol, the greater part of the vacuole content may be expressed without rupturing the leaf-cells. The remainder may be extracted by repeatedly treating the residues with very dilute hydrochloric acid (0.002 N) and again

expressing; dilute acid is used in place of water since the latter would dissolve some of the protoplasmic protein. The residue from the hydrochloric acid extract contains the protoplasmic material, which may be extracted by grinding with water. The method has been applied to spinach leaves.

E. S.

**The Role of Vitamins in Cell Chemistry.** W. R. HESS (*Z. physiol. Chem.*, 1923, 127, 196—198; cf. A., 1922, i, 399; Abderhalden, *ibid.*, i, 607).—It is claimed that Abderhalden's results do not disprove the author's conclusion that vitamin-B probably acts as a biocatalyst in cell oxidation processes.

W. O. K.

**Assimilation of Electrolytes by Plants. I.** SILVESTRÉ PAIS (*Biochem. Z.*, 1923, 136, 366—376).—By determination of the electrical conductivity of nutrient solutions, the steady fall of concentration through absorption by growing plants can be followed quantitatively. Resorption of electrolytes depends on the intensity of the growth and is little affected by the transpiration. Using pure solutions ( $M/100$ ) of sodium and potassium chlorides, it is found that the concentration of these salts is unchanged in the absorbed water whilst magnesium and calcium chlorides are taken up in lesser concentrations.

H. K.

**Synthesis of Acid Amides in Plants through Nourishing with Ammonium Salts.** A. I. SMIRNOV (*Biochem. Z.*, 1923, 137, 1—34).—Etiolated plant shoots of barley grains rich in carbohydrates show a pronounced assimilation of nitrogen as ammonia, as is proved by the increased amide nitrogen content (attributed to formation of asparagine). The rate of this assimilation is greatest on the first day and falls off thereafter through the disappearance of carbohydrates. Calcium salts exert a favourable influence. The etiolated shoots of seeds with a low reserve of carbohydrates, such as lupines, take up ammonium salts in the presence of dextrose, but less so than do barley grains in the absence of dextrose. Methods are described for the pure culture of higher plants under sterile conditions.

H. K.

**Chemical Constituents of Green Plants. XXVII. Succinic Acid.** HARTWIG FRANZEN and RUDOLF OSTERTAG (*Biochem. Z.*, 1923, 136, 327—335).—From a critical survey of the literature, it is concluded that out of thirty-three plants in which succinic acid is stated to occur, it occurs certainly in ten and probably in another three.

H. K.

**Protein Precipitation in Grasses.** MARGARET H. O'DWYER (*Proc. Linnean Soc. New South Wales*, 1922, 47, 513—515; cf. Petrie, *ibid.*, 1908, 33, 837; Chibnall and Schryver, A., 1921, i, 482; Buston and Schryver, A., 1922, i, 182).—Comparison of the precipitation of proteins by Stützer's reagent, tannin-sodium chloride solution, 94% alcohol, and Barnstein's method with Australian grasses appears to support Petrie's statement that Stützer's reagent precipitates some of the non-protein nitrogen.

CHEMICAL ABSTRACTS.

**The Chemical Constituents of Green Plants. XXV. The acids of the Apple (*Pyrus malus*).** HARTWIG FRANZEN and RITZ HELWERT (*Z. physiol. Chem.*, 1923, 127, 14—38).—By the use of the ester-hydrazide method, it is shown that malic acid is the most important acid of the apple, and that there are also present quantities of citric acid besides small amounts of succinic and of acetic acid and traces of oxalic and of unsaturated acids.

W. O. K.

**Chemical Constituents of a Chinese Drug "Hsiung-huang."** II. YOSHIHARU MURAYAMA and TAKEYOSHI ITAXI (*J. Pharm. Soc. Japan*, 1923, 143—148; cf. A., 1922, i, 310).—In addition to the main constituent enidiolactone (*loc. cit.*), the volatile oils obtained by distilling the powdered drug with steam contains also a small quantity of sedanonic acid, m. p. 113° (the xime, needles, has m. p. 128°), and a sesquiterpene, a light yellow oil, b. p. 110—120°/5 mm., which gives a coloration changing from dark green to violet-red with acetic anhydride and concentrated sulphuric acid.

K. K.

**The Relationship of Cotton to Water and Steam. A Summary of the Literature.** ROBERT GEORGE FARGHER and ALEXANDER MITCHELL WILLIAMS (*J. Text. Inst.*, 1923, 14, T., 77—82).—A review of the literature, divided into the following chapters: 1) removal of the minor constituents of cotton by water, (2) chemical action of water and steam on cellulose, (3) general humidity relations, (4) physical effects of moisture content, (5) effect of steam on the appearance of cotton, (6) other effects. Fifty-eight references are cited.

J. C. W.

**A Comparison of the Volatile Products Derived from Cotton by the Action of Water, and of Sodium Hydroxide, and 2.7 Atmos. Pressure.** PERCY HERBERT CLIFFORD and ROBERT GEORGE FARGHER (*J. Text. Inst.*, 1923, 14, T., 117—124).—The material employed in the investigation was obtained by condensing the steam issuing from a kier in which raw American cotton was heated under 2.7 atmos. pressure, either with water or 2% sodium hydroxide solution. Several gallons of distillate were collected, the quantity of cotton used being a few tons. The systematic isolation of the products is fully described.

The distillate from sodium hydroxide contained the following compounds. (1) Neutral products: Acetone; methyl alcohol; a trace of a compound,  $C_6H_{12}O_2$ , giving a p-nitrophenylhydrazone, m. p. 210°; a colourless aldehyde or ketone,  $C_{10}H_{20}O$ , which rapidly became yellow and formed a semicarbazone, m. p. 116—116.5°; and a compound,  $C_{18}H_{30}O$ , which had a pleasant, camphor-like odour, and was indifferent to reagents for carbonyl or hydroxyl groups. The last two compounds were obtained together as a small quantity of oil, b. p. 90—140°/2 mm., and were separated by distillation in steam, the indifferent compound being the more volatile. (2) Volatile bases: Ammonia; trimethylamine (the picrate has m. p. 224°, not 216° as usually given); dimethylamine (the hydrogen oxalate, has m. p. 149—150°); and a pyrrolic substance.

The distillate from water alone contained acetaldehyde, but not methyl alcohol, the other neutral products being similar to those obtained from sodium hydroxide. A quantity of the aqueous extract in the kier was evaporated under diminished pressure, extracted with ether and chloroform, and acidified, when a jelly was obtained which yielded methyl alcohol and acetone on distillation with sodium hydroxide. The methyl alcohol appears to come, therefore, from a substance which is removed from the cotton by boiling with water, and not from the residual cotton.

The evidence afforded by the distribution of methyl alcohol and acetone in the distillates therefore strongly supports the view that raw cotton contains pectin, which has hitherto been somewhat doubtful.

A separate small experiment in which cotton was treated with 1% sodium hydroxide showed that 100 g. of cotton yielded 14 mg. of acetone and 4 mg. of methyl alcohol, that is, two molecular proportions of acetone to one of methyl alcohol. J. C. W.

**Chemical Investigations of the Fruit of *Evodia Rutecarpa*.** YASUHIKO ASAHINA [with M. ISHIO, K. KASHIWAGI, S. MAYEDA, and A. FUJITA] (*Acta Phytochim.*, 1923, **1**, 67—89).—A reprint in German of a series of papers previously published in Japanese (cf. A., 1916, i, 238, 621; 1921, i, 48; 1922, i, 47). Kermack, Perkin, and Robinson (T., 1921, **119**, 1615) have criticised the conclusion that the base  $C_{10}H_{12}N_2$  from isoevodiamine is 2- $\beta$ -aminoethylindole, suggesting that it is more probably 3- $\beta$ -aminoethylindole. Physiological experiments in which the base was compared with 3- $\beta$ -aminoethylindole show, however, that the two are quite different. E. H. R.

**Distribution of Pentosans in the Maize Plant at Various Stages of Growth.** JOHN H. VERHULST, W. H. PETERSON, and E. B. FRED (*J. Agric. Res.*, 1923, **23**, 655—663).—Chemical examination of maize plants of various ages shows that the amount of pentosans in the plant increases with the total dry matter, being approximately one-sixth of the dry matter. In the early stages of growth, the production of pentosans in the plant-tissue is greater than that of dry matter; its formation from starch, etc., is suggested. The percentage of pentosan in particular organs of the plant increases with the development of that organ. Only traces of methyl pentosans were found, but pentoses were found in small but regular quantities throughout the plant's growth.

The pentosans in green corn tissue are destroyed by *Bacillus flavigina*, and also by *B. coli communis*. A. G. P.

**Mannitol from *Orobancha Cumana*.** A. KIESEL (*Z. physiol. Chem.*, 1923, **126**, 257—260).—The substance, m. p. 165°, obtained from *Orobancha Cumana* by extraction with alcohol is shown to be mannitol. W. O. K.

**The Presence of Aucubin and of Mannitol in the Foliated Stems of *Rhinanthus Crista-Galli*, L.** (Mlle) MARIE BRACKER (*Bull. Soc. Chim. biol.*, 1923, **5**, 258—262).—Aucubin is present

the foliated stems as well as in the seed (cf. A., 1922, i, 1225). Mannitol, but not dulcitol, has also been isolated. E. S.

**The Chemical Constituents of the Rutaceæ. VII. The White Dittany, *Dictamnus albus*, Linn.** H. THOMS (*Ber. Deut. Pharm. Ges.*, 1923, 33, 68—83).—A hot 85% alcoholic extract of dittany root deposited a saponin on cooling, and, after concentrating on a water-bath to a syrupy extract, crystals were deposited which after recrystallisation from alcohol melted at 279—280° and had the composition  $C_{16}H_{18}O_5$ . The substance possessed a zwitterionic character, and was named *dictamnolactone*. No methoxyl- or acetyl-derivatives, oximes, or semicarbazones could be obtained, and bromine gave a substitution product. The general behaviour of the substance indicated a cyclic structure, probably similar to that of santonin. In the residual extract from which the dictamnolactone had been separated the presence of sucrose, invert-sugar, pentose, an ethereal oil, a waxy substance, a phenolcarboxylic acid, and an alkaloid was established. The alkaloid *dictaminine*,  $C_{17}H_{17}O_4N$ , crystallised from absolute alcohol in colourless prisms, m. p. 132—133°. It formed a sparingly soluble chromate, and a chloroaurate and chloroplatinate, the latter melting at 152°.

G. F. M.

**Soil Acidity as Measured by Sugar Inversion, the Truog Test, and the Hydrogen-ion Concentration and its Relation to the Hydrolysis of Ethyl Acetate.** F. W. PARKER and O. C. BRYAN (*Soil Sci.*, 1923, 15, 99—107).—The reaction of a number of soils was determined by the above three methods and compared with the acidity developed by shaking soil suspensions with ethyl acetate. A fairly good correlation appeared to exist between the three standard methods, the Truog test and sugar-inversion showing the best parallelism. It was shown that acid silicates catalyse the inversion of sucrose, and probably are the main factor in the sugar inversion by soils. The hydrolysis of ethyl acetate by soil suspensions was not catalysed by acid silicates. A. G. P.

**Relations between Calcium Carbonate, certain Fertiliser Chemicals, and the Soil Solutions.** FRED. W. MORSE (*Soil Sci.*, 1923, 15, 75—92).—The results of published data are discussed and interpreted mathematically, and analyses of water extracts of soils from limed and fertilised plots given. In soils containing solid calcium carbonate, the quantity actually in solution is dependent solely on the proportion of carbon dioxide in the soil atmosphere. The addition of calcium phosphate and sulphate and of ammonium sulphate tends to decrease the amount of calcium carbonate in the soil solution. Sodium nitrate and potassium chloride have the reverse effect. The  $p_H$  value of extracts from limed plots is scarcely altered by treatment with superphosphate and potassium chloride. Ammonium sulphate lowers the  $p_H$  value of the extracts and sodium nitrate increases it. A. G. P.

**The Manganese Content of some Dutch Soils, and some Observations Thereon.** D. H. WESTER (*Pharm. Weekblad*, 1923, 60, 446—451).—Manganese found in the dried soils by the methods previously described (A., 1920, ii, 451) varied from a trace up to 120 mg. per 100 g. of dried soil. The more fertile soils contain more manganese than the less fertile, but no connexion is found between the contents of iron and manganese, although some connexion between manganese and phosphate content in some localities is not unlikely. The manganese content of the ash of leaves and seeds is generally much higher than that of the soils.  
S. I. L.

**The Quantity and Composition of Colloidal Clay in Soil.** VÁCLAV NOVÁK and LAD. ŠMOLÍK (*Kolloid Z.*, 1923, 32, 338—343).—A number of experiments are described which have been undertaken with the object of ascertaining the quantity of colloidal clay in two specimens of agricultural earth and in one specimen of clay poor in humus derived from a clay-slate. The total quantity of colloidal material, including the humus substances, in agricultural earth, when dispersed in an ammoniacal solution, probably exceeds 8%. The quantity of inorganic colloidal matter, that is, colloidal alumina, is probably somewhat greater than 5%. Three specimens of iron containing colloidal clays have been analysed and found to contain large amounts of alkalis and alkaline earths.  
J. F. S.

**The Interpretation of Mechanical Analysis of Soils as Affected by Soil Colloids.** R. O. E. DAVIS (*J. Amer. Soc. Agron.*, 1922, 14, 293—298).—The application of a correction, expressing the amount and distribution of soil colloids, to the results of mechanical analysis is essential, especially in the case of the silt and clay groups. These groups of mineral particles are composed in part of colloidal material which may be estimated by absorption of water vapour.  
CHEMICAL ABSTRACTS.

**Organic Constituents of the Soil.** G. S. FRAPS (*Texas Agr. Exp. Sta. Bull.*, 1922, 300, 1—10).—Estimations are compared of the organic carbon, nitrogen, and pentosans in a number of surface- and sub-soils. The estimation of organic carbon gives little indication of the quality of a soil; the percentage can be judged from that of the nitrogen. The average amount of pentosans increases with the average nitrogen content. The rate of disappearance in soil of pentosans from various sources was found to vary widely. The amount of reducing substance, calculated as sugars, produced by heating soils with dilute sulphuric acid was 0.002—0.215% (average 0.058%). No relation could be found between the permanganate-soluble and -insoluble nitrogen, and the results of pot experiments with nitrogen on soils. An average of 10% of the nitrogen of soils was dissolved by 0.1N-potassium hydroxide solution.  
CHEMICAL ABSTRACTS.

## Organic Chemistry.

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**Partial Combustion of Methane.** E. BERL and H. FISCHER (*Z. angew. Chem.*, 1923, **36**, 297—302).—The possibility of oxidising methane to methyl alcohol, formaldehyde, formic acid, carbon monoxide, and carbon dioxide by means of oxygen, ozone, sulphur dioxide, and sulphur trioxide, and the effect of temperature on the various reactions occurring are discussed from a theoretical point of view based on the heats of possible reactions. Investigations were made oxidising methane with air between 500° and 900°, gaseous mixtures of various compositions being passed through heated tubes not containing catalysts, and the products collected and analysed. Experiments with sulphur dioxide and sulphur trioxide were carried out between 250° and 800°, using silica as catalyst. Some qualitative experiments were also performed with nitrogen peroxide. Using an equal volume of air at 675°, under the conditions of the experiments 17% of the methane consumed was obtained as formaldehyde, the remainder appeared as carbon monoxide. With sulphur dioxide, most of the methane oxidised formed carbon dioxide, using sulphur trioxide with a large excess of methane at 595°, the small quantity of methane oxidised gave formaldehyde and nothing else. Nitrogen peroxide yields formaldehyde with other products. Experiments on the stabilisation of formaldehyde with ammonia showed that substance to be of little utility.

T. S. W.

**The Possibility of Using Chlorosulphonic Acid to Absorb Ethylene from Gaseous Mixtures.** W. TRAUBE and R. JUSTH (*Brennstoff-Chem.*, 1923, **4**, 150—154).—Although the absorption of ethylene in bromine water or fuming sulphuric acid is satisfactory for analytical purposes, the products formed do not readily yield derivatives of ethylene of technical value. Experiments made with chlorosulphonic acid showed that this substance gives an absorption of ethylene almost as rapid and complete as 25% fuming sulphuric acid, whilst if the chlorosulphonic acid be mixed with an equal or twice its weight of pure sulphuric acid the reagent obtained can replace the fuming sulphuric acid in even the most accurate analyses. Experiments were also carried out on the effect of passing gases containing ethylene through chlorosulphonic acid. It was found that even with rapid currents of gas of the order of 1 litre in one minute nearly 90% of the ethylene is absorbed in one washing from gas containing 7% of ethylene. Only 6% absorption was obtained with concentrated sulphuric acid under the same conditions. The compound formed with the chlorosulphonic acid is its ethyl ester, b. p. 155—160°, which remains condensed to a very small extent only; this small amount can be removed from the gas by means of activated charcoal. Only

80% of the theoretical amount of ethylene is absorbed by the pure acid owing to some of the latter reacting with its ethyl ester to form an ethionic acid derivative,  $\text{SO}_2\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_3\text{H}$ . Ethyl chlorosulphonate can yield several products of technical value, e.g., with water it gives alcohol, and with concentrated hydrochloric acid ethyl chloride.

T. S. W.

**The Question of Atomic Equilibria in Molecules of Hydrocarbons of the  $\text{C}_n\text{H}_{2n-2}$  Series.** ALEXEI EUGRAPOVITSCH FAVORSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 557—570).—It was shown some years ago that monosubstituted acetylenes isomerise under the influence of alcoholic alkalis (A., 1888, 798); disubstituted acetylenes are produced if the original substituent is a primary group, the intermediate formation of an allene derivative being assumed:  $\text{CH}_3\text{R}\cdot\text{C}\equiv\text{CH} \rightarrow \text{CHR}\cdot\text{C}\equiv\text{CH}_2 \rightarrow \text{CHR}\cdot\text{C}=\text{CH}_2$ . The reaction stops at the allene stage, if the substituent is a secondary group,  $\text{CHRR}'\cdot\text{C}\equiv\text{CH} \rightarrow \text{CRR}'\cdot\text{C}\equiv\text{CH}_2$ , whilst acetylenes carrying a tertiary group as a substituent are not isomerised. Recently, however, it was found that  $\delta\delta$ -dimethyl- $\Delta^8$ -pentinene,  $\text{CMe}_3\cdot\text{C}\equiv\text{CMe}$ , is not produced by the action of sodium ethoxide on  $\alpha\beta$ -dibromo- $\gamma\gamma\gamma$ -tetramethylpropane, the product being  $\delta\delta$ -methyl- $\Delta^8$ -pentadiene,  $\text{CMe}_3\cdot\text{CH}\cdot\text{C}\equiv\text{CH}_2$ . It is now suggested that the above scheme must be extended. When R is a primary group the formation of the disubstituted acetylene proceeds to completion; when R is a tertiary radicle, as in the above example, it is the allene derivative which is alone capable of existence, whilst when R is a secondary radicle both forms possess approximately equal stability.

The formation of the allene derivative appears to be due to the instability of the isomeric dimethylpentinene; this view is confirmed by the attempts to synthesise the latter, the allene being obtained in its place.

[With OLGA ALEXÉEVA.]—Ethyl*tert*-butylcarbinol was converted into the corresponding bromohydrin,  $\alpha$ -bromo- $\alpha$ -*tert*-butylpropane, and the elements of hydrogen bromide were removed from this compound by means of alcoholic potash. The product consisted of a mixture of two hydrocarbons which were separated by fractionation. The fraction boiling at  $84$ – $86^\circ$ ,  $d_4^{20}$  0.7414;  $d_4^{20}$  0.7230, gives acetic and  $\alpha\alpha$ -dimethylpropionic acids on oxidation, and is therefore  $\alpha\alpha$ -dimethyl- $\Delta^8$ -pentinene,  $\text{CHMe}\cdot\text{C}\equiv\text{CMe}_3$ , whilst the fraction, b. p.  $93$ – $95^\circ$ , consists of  $\beta\gamma$ -dimethyl- $\Delta^8$ -pentinene,  $\text{CMe}_3\cdot\text{CMeEt}$ ,  $d_4^{20}$  0.7553,  $d_4^{20}$  0.7363; on oxidation, acetone, methyl ethyl ketone and  $\beta\gamma$ -dimethylpentane- $\beta\gamma$ -diol (Meerwein, A., 1913, i, 485) are obtained from it. The hydrocarbon boiling at  $84$ – $86^\circ$  was converted by means of bromine in chloroform into the dibromide, b. p.  $86$ – $88^\circ/15$  mm.,  $d_4^{20}$  1.5530,  $d_4^{20}$  1.5303, and this was treated with an excess of alcoholic potassium hydroxide, giving an 89 per cent. yield of  $\delta\delta$ -dimethyl- $\Delta^8$ -pentadiene (*tert*-butylallene), b. p.  $81$ – $82.5^\circ$ ,  $d_4^{20}$  0.7365,  $d_4^{20}$  0.7183,  $[R]_D^{20}$  33.63. On oxidation with permanganate, it yields formic and  $\alpha\alpha$ -dimethylpropionic acids.

The course of the reaction here is as follows:  $\text{CMe}_3\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_3 \rightarrow \text{CMe}_3\cdot\text{CH}\cdot\text{CBr}\cdot\text{CH}_3 \rightarrow [\text{CMe}_3\cdot\text{C}(\text{C}\cdot\text{CH}_3)] \rightarrow \text{CMe}_3\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2$ , which was confirmed as follows:  $\delta\delta$ -dimethyl- $\Delta^2$ -pentinene, obtained from pinacolin, was converted into the sodium derivative, and this was heated with an excess of methyl iodide in a sealed tube for eight hours at  $120^\circ$ . The hydrocarbon isolated boiled at  $81-83^\circ$ ,  $d_4^{20}$  0.7363,  $d_4^{20}$  0.7182,  $[\text{R}_L]_D$  33.056, and was thus identical with  $\alpha$ -butylallene; its structure was confirmed by oxidation.

G. A. R. K.

**The Metallic Derivatives of *tert*.-Butylacetylene [ $\delta\delta$ -Dimethyl- $\Delta^2$ -pentinene].** A. E. FAVORSKI and LEONID MOREV (*Russ. Phys. Chem. Soc.*, 1920, **50**, 571-581).—The copper derivative of the hydrocarbon,  $\text{CMe}_3\cdot\text{C}\cdot\text{CH}$ , which was prepared from pinacolin (cf. A., 1888, 798) occurs in two polymeric modifications, red crystals, and a yellow, amorphous powder or plate-like crystals. The yellow form appears to pass into the red on warming at about  $80^\circ$ ; both forms melt at about  $140^\circ$ . A third, orange form may also exist.

Cryoscopic determinations show that the molecular weight of the yellow modification is higher than that of the red, the values in the solution of either form in benzene being lower than those found in ether. On keeping the solutions, the molecular weight gradually falls until it nearly reaches the theoretical value for the bimolecular compound; decomposition appears to set in at that point. Heating also favours the dissociation of these compounds. By crystallising the substance from benzene, it is possible to transform the yellow modification into the red, and the reverse change is brought about by chloroform. On prolonged keeping of the solutions of either modification, gradual decomposition takes place, a gummy solid being deposited consisting of a colloidal form of copper. Such a decomposition can be brought about by heating the dry yellow modification in a tube at  $150^\circ$ , when a copper mirror is formed and a white sublimate of the dimeric form of  $\alpha\alpha$ -dimethyl- $\beta$ -pentinene, m. p.  $130-131^\circ$ , collects on the cool parts of the tube.

On oxidation with alkaline potassium ferricyanide, the copper salt yields the same dimeric compound, m. p.  $130-131^\circ$ , in addition to some  $\beta\beta$ -dimethylbutyric acid, b. p.  $176-178^\circ$ .

The silver compound of dimethylpentinene is colourless, and crystallises from benzene in fine needles. The benzene solutions on keeping deposit a silver mirror.

The constitution of the polymeric forms of the copper compound is discussed, and their formation is attributed to the residual finity of the trebly-bound carbon atoms and that of the singly-bound copper.

G. A. R. K.

**Action of Potassium Acetate on Aliphatic Bromides as a Method of Determining Constitution.** I. B. K. MERESHKOVSKY (*Annalen*, 1923, **431**, 231-242).—From existing data and the experimental results indicated below, it is concluded that the action of potassium acetate on aliphatic bromides proceeds according to the following rules. I. Monobromides. Bromine is removed

from primary or secondary carbon with formation of an acetic ester, from tertiary carbon with formation of an unsaturated hydrocarbon, a hydrogen atom being taken from the carbon atom bearing fewest hydrogen atoms. II. Dibromides. (1) Diprimary dibromides give esters of the corresponding glycols. (2) Primary-secondary dibromides give (a) unsaturated monobromides, in which bromine remains on the primary carbon atom, and (b) glycol diacetates. Dissecondary dibromides behave similarly. (3) Primary-tertiary dibromides give exclusively unsaturated monobromides, with bromine on the primary carbon. Secondary-tertiary dibromides react in the same way, bromine remaining on the secondary carbon. (4) Ditertiary dibromides give doubly unsaturated hydrocarbons. If the bromine atoms are attached to neighbouring carbon atoms, the ester of the unsaturated alcohol may be isolated as an intermediate product. III. Tribromides. (1) Diprimary-secondary tribromides lose bromine from a primary carbon atom, giving an unsaturated bromo-ester,  $\text{CH}_2\text{:CBr} \dots \text{CH}_2\text{-OAc}$ . (2) Diprimary-tertiary tribromides give unsaturated mono-esters, the third bromine atom being left on a primary carbon atom,  $\text{CHBr:C<}$ . (3) From dissecondary-primary tribromides only unsaturated 1:2-dibromides are formed. (4) Tribromides with two bromine atoms on primary carbon and one on tertiary carbon give unsaturated dibromides,  $\text{CBr}_2\text{:C<}$ . (5) Tribromides having two bromine atoms on one primary carbon atom and one on secondary carbon give a mixture of unsaturated dibromides, the 1:2-dibromide predominating,  $\text{CHBr:CBr-}$ ,  $\text{CBr}_2\text{:CH-}$ . IV. Tetrabromides react according to the schemes for dibromides and tribromides. Bromine attached to unsaturated carbon does not react. By the elimination of hydrogen bromide from a 1:2-dibromide the double bond remains next to the remaining bromine atom, e.g.,  $\text{-CBr:C<}$ , and not  $\text{-CHBr:C=C<}$ . If the halogen atoms in the bromide are removed from one another, each reacts as though it alone were present in the molecule. It is probable that the acetic ester is invariably the initial stage in the formation of an unsaturated product.

$\beta$ -Bromoisobutane is converted by heating with anhydrous potassium acetate and glacial acetic acid into isobutylene. Dimethylbutene dibromide,  $\text{CMe}_2\text{Br-CMe}_2\text{Br}$ , gives  $\beta\gamma$ -dimethyl- $\Delta^2$ -butadiene,  $\text{CH}_2\text{:CMe-CMe:CH}_2$ , and the ester,  $\text{OAc-CMe}_2\text{:CMe}_2\text{-OAc}$ . The observation of Bainbridge (T., 1914, 105, 2291), that  $\alpha\beta$ -dibromopropane gives  $\alpha$ -bromopropylene is confirmed; the glycol diacetate,  $\text{OAc-CHMe-CH}_2\text{-OAc}$ , is also formed.  $\alpha\beta\gamma$ -Tribromopropane is converted into the triacetate (Wurtz, *Annalen*, 1857, 102, 340), and the ester,  $\text{CH}_2\text{:CBr-CH}_2\text{-OAc}$ , b. p.  $103.5^\circ/100$  mm. or  $163\text{--}164^\circ/762$  mm.,  $d_4^{20}$  1.48894,  $d_4^{30}$  1.45668,  $n_D^{20}$  1.466572 (cf. Henry, A., 1872, 686), which is also produced by heating  $\beta\gamma$ -dibromopropylene with potassium acetate.  $\alpha\alpha\beta$ -Tribromopropylene (cf. Reboul, A., 1879, 127; Mounicyrat, A., 1899, i, 97), b. p.  $89.2^\circ/20$  mm.,  $d_4^{20}$  2.39384,  $d_4^{30}$  2.35484,  $n_D^{20}$  1.57016,  $n_D^{30}$  1.573983,  $n_D^{20}$  1.58470,  $n_D^{30}$  1.593719, gives a small amount of  $\alpha\alpha$ -dibromopropylene,  $\text{CHMe:CBr}_2$ , b. p.  $123\text{--}126^\circ/759$  mm., and, as the chief

product,  $\alpha\beta$ -dibromopropylene,  $\text{CMeBr}\cdot\text{CHBr}$ , b. p.  $129-130^\circ/759$  mm.,  $d_4^{20}$  2.04558,  $d_4^{25}$  2.00768,  $n_D^{20}$  1.52618,  $n_D^{25}$  1.529992,  $n_D^{30}$  1.53987,  $n_D^{40}$  1.549323 (cf. Linnemann, *Annalen*, 1863, **136**, 57).  $\alpha\beta$ -Dibromopropylene is also formed by the action of potassium acetate on  $\alpha\beta$ -tribromopropane, b. p.  $80.6^\circ/20$  mm.,  $d_4^{20}$  2.33690,  $d_4^{25}$  2.29854,  $n_D^{20}$  1.56247,  $n_D^{25}$  1.566963,  $n_D^{30}$  1.577794,  $n_D^{40}$  1.585556 (cf. Reboul, *loc. cit.*). Revised physical data are given for the ester,  $\text{CBr}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$  (this vol., i, 528), derived from  $\alpha\alpha\beta\gamma$ -tetrabromoisobutane:  $d_4^{20}$  1.77845,  $d_4^{30}$  1.75001,  $n_D^{20}$  1.513898,  $n_D^{30}$  1.517607,  $n_D^{40}$  1.527015,  $n_D^{50}$  1.53509, and for the corresponding alcohol,  $\text{CBr}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$ , m. p.  $31^\circ$ ,  $d_4^{20}$  2.02099,  $d_4^{30}$  1.99193,  $n_D^{20}$  1.556423,  $n_D^{30}$  1.560942,  $n_D^{40}$  1.571956,  $n_D^{50}$  1.580662. W. S. N.

**Bromotrinitromethane. II.** ERICH SCHMIDT, RICHARD SCHUMACHER, and RICHARD ASMUS (*Ber.*, 1923, **56**, [B], 1239—1242; cf. A., 1922, i, 826).—During attempts to add the ester of hypobromous acid to the olefinic double linking by means of bromotrinitromethane in alcoholic solution, it has been found that treatment with alkali is unsuitable for compounds containing a labile halogen atom. The difficulty can be overcome by the use of potassium ferrocyanide in acetic acid solution (cf. Chattaway and Harrison, T., 1916, **109**, 171).

Bromotrinitromethane may also be brought into reaction with the olefinic double linking in the presence of acids, particularly formic acid, thus:  $\cdot\text{CH}:\text{CH}\cdot + \text{HO}\cdot\text{CHO} + \text{CBr}(\text{NO}_2)_3 \rightarrow \text{CH}(\text{O}\cdot\text{CHO})\cdot\text{CHBr} + \text{CH}(\text{NO}_2)_3$ .

*Bromomethoxyhydrindene*,  $\text{C}_9\text{H}_8\text{Br}\cdot\text{OMe}$ , a pale yellow liquid, b. p.  $98^\circ/2$  mm., is obtained in 71.9% yield by the gradual addition of bromotrinitromethane to an ice-cold solution of freshly distilled indene in methyl alcohol.

The addition of cyclohexene to a solution of carbamide and bromotrinitromethane in formic acid results in the production of *2-bromocyclohexanyl formate*,  $\text{C}_6\text{H}_{10}\text{Br}\cdot\text{O}\cdot\text{CHO}$ , a colourless liquid, b. p.  $68-69^\circ/0.5$  mm., the yield being 70% of that theoretically possible. It is converted by methyl alcohol and hydrochloric acid into *2-bromocyclohexane-1-ol*, a colourless liquid which gradually darkens when preserved, b. p.  $60-61^\circ/\text{about } 1$  mm. In a similar manner, propenylbenzene gives  $\beta$ -bromo- $\alpha$ -formoxypropylbenzene,  $\text{CHMeBr}\cdot\text{CHPh}\cdot\text{O}\cdot\text{CHO}$ , a colourless liquid, b. p.  $104^\circ/1$  mm., in 49.4% yield, whereas camphene gives *O-formylcamphenebromohydrin*,  $\text{C}_{10}\text{H}_{16}\text{Br}\cdot\text{O}\cdot\text{CHO}$ , a colourless liquid, b. p.  $109-111^\circ/0.6$  mm., the yield being 73.5% of that theoretically possible.

H. W.

**Examination and Dehydration of Methyl Alcohol with the Aid of Magnesium.** NIELS BJERRUM and LÁSLÓ ZECHMEISTER (*Ber.*, 1923, **56**, [B], 1247; cf. this vol., i, 529).—The molecular conductivity of picric acid dissolved in methyl alcohol which has been dehydrated by means of magnesium is identical with that observed in the solvent which has been treated with calcium.

H. W.

**The Purification and some Physical Properties of certain Aliphatic Alcohols. II.** ROGER F. BRUNEL (*J. Amer. Chem. Soc.*, 1923, 45, 1334—1338; cf. A., 1921, i, 299).—The thermometer previously used has been recalibrated, and used to determine the boiling points of various aliphatic alcohols and ketones.

*n*-Propyl alcohol, obtained by the hydrolysis of pure propyl hydrogen phthalate, has b. p.  $97.175 \pm 0.01^\circ/760$  mm.,  $d_4^{25}$  0.7998,  $n_D^{25}$  1.3834. *iso*Propyl alcohol has b. p.  $82.258 \pm 0.005^\circ/760$  mm.,  $d_4^{25}$  0.7808,  $n_D^{25}$  1.3748, and is obtained by the reduction of pure acetone, b. p.  $56.085 \pm 0.01^\circ/760$  mm. *sec.*-Butyl alcohol has b. p.  $99.529 \pm 0.005^\circ/760$  mm.,  $d_4^{25}$  0.8023,  $n_D^{25}$  1.39495, and is prepared by the reduction of pure methyl ethyl ketone, b. p.  $79.370 \pm 0.01^\circ/755$  mm. The following data are also given. Methylisobutylcarbinol, b. p.  $131.85 \pm 0.01^\circ/760$  mm.,  $d_4^{25}$  0.80245,  $n_D^{25}$  1.40895. Methylpropylcarbinol, b. p.  $119.275 \pm 0.01^\circ/754$  mm.,  $d_4^{25}$  0.80483,  $n_D^{25}$  1.4043. Diethylcarbinol, b. p.  $115.40 \pm 0.01^\circ/754$  mm.,  $d_4^{25}$  0.8154,  $n_D^{25}$  1.4077. Dipropylcarbinol, b. p.  $155.00 \pm 0.01^\circ/750$  mm.,  $d_4^{25}$  0.8129,  $n_D^{25}$  1.4178. W. S. N.

**Action of Magnesium Halides on the Epibromohydrin of Ethylglycerol.** RAYMOND DELABY (*Compt. rend.*, 1923, 176, 1326—1327; cf. this vol., i, 531).—A study of the action of magnesium chloride and magnesium bromide on the epibromohydrins of ethyl- and butyl-glycerol showed that, in order to bring about the reaction described by Würtz (*Compt. rend.*, 1860, 50, 1197) with the resultant precipitate of magnesium hydroxide, the materials used should be quite pure. Certain experimental aspects of the reaction are discussed and the optimum conditions are indicated.

H. J. E.

**Tetramethylglycerol.** J. PASTUREAU and H. BERNARD (*Compt. rend.*, 1923, 176, 1400—1402; cf. A., 1922, i, 717).—Saponification of the chlorohydrin of tetramethylglycerol affords a better yield than the preparation by means of the acetin. Tetramethylglycerol [ $\beta\delta$ -dimethylpentane- $\beta\gamma\delta$ -triol],  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$ , was obtained in the form of brilliant needles, m. p.  $99^\circ$ . An attempt to prepare the glycide,  $\text{Me}_2\text{C}=\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$ , resulted in the formation of a small quantity of colourless liquid which was readily hydrolysed to tetramethylglycerol.

H. J. E.

**Solubility of Mannitol in Mixtures of Ethyl Alcohol and Water.** HENRY JERMAIN MAUDE CREIGHTON and DAVID S. KLAUDER (*J. Franklin Inst.*, 1923, 195, 687—691).—Within the temperature range  $0$ — $60^\circ$ , the logarithm of the solubility of mannitol in mixtures of ethyl alcohol and water at any temperature is a function of the solubility in pure water, the molar fraction of alcohol present in the solvent, and the absolute temperature; whilst at a particular temperature it is a function of the solubilities in the pure component solvents and the molar fractions of the latter.

E. E. T.

**The Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid.** CYRIL NORMAN HINSHELWOOD and HAROLD HARTLEY (T., 1923, 123, 1333—1338).

**The Decomposition of Pertrichloroacetic Acid.** FR. FICHTER, LEBERT FRITSCH, and PAUL MÜLLER (*Helv. Chim. Acta*, 1923, 6, 2—506).—When a salt of trichloroacetic acid is electrolysed, no hane derivative is formed, but exclusively the ester, trichloroethyl trichloroacetate. This behaviour resembles that of *cyclohexanecarboxylic acid* (this vol., i, 677), and should be explainable a similar way through the formation of trichloromethyl alcohol y the decomposition of pertrichloroacetic acid formed at the node. To study its decomposition, the latter was prepared by ixing trichloroacetic anhydride and hydrogen peroxide and heating the mixture in such a manner that the gaseous decomposition roducts could be collected and analysed. The decomposition as found to proceed according to the equation  $\text{CCl}_3\cdot\text{CO}_2\cdot\text{OH} = \text{O}_2 + \text{COCl}_2 + \text{HCl}$ , probably through the stages  $\text{CCl}_3\cdot\text{CO}_2\cdot\text{OH} = \text{O}_2 + \text{CCl}_2\cdot\text{OH}$  and  $\text{CCl}_2\cdot\text{OH} = \text{COCl}_2 + \text{HCl}$ . The formation of ichloromethyl alcohol as an intermediate product in the electrolysis of a trichloroacetate is consequently extremely probable. n attempt to prepare trichloroacetyl peroxide by the action of arium peroxide on trichloroacetic anhydride was unsuccessful; he compound apparently cannot exist. E. H. R.

**A New Source of Ceryl Cerotate.** ADOLF BAREUTHER (*Chem. Umschau*, 1923, 30, 117—119).—The bottom layers of sunflower il from a tank which had been used for its storage were found o become cloudy and gelatinous after refining owing to the presence f ceryl cerotate, which was held in solution in the crude oils by the ree fatty acids present. The wax was found to originate from the usks of the sunflower seeds, and had gradually concentrated in he bottom layers of oil. 42 G. of the crude wax were isolated rom 30 kg. of oil (=0.14%). The wax was purified by recrystallisation from chloroform, and both ceryl alcohol and cerotic acid ere prepared from it. H. C. R.

**γ-Oxalyl Derivatives of ββ- and αβ-Dimethylacrylic Acids.** LUCY HIGGINBOTHAM and ARTHUR LAPWORTH (T., 1923, 123, 325—1332).

**The Highly Unsaturated Fatty Acids of Fish Oils.** J. B. BROWN and G. D. BEAL (*J. Amer. Chem. Soc.*, 1923, 45, 1289—303).—The mixed fatty acids of menhaden oil undergo an increase in molecular weight, as shown by titration, when heated at 240° in a current of carbon dioxide, but the esters can be distilled almost without decomposition. Menhaden oil is esterified by means of alcoholic hydrogen chloride, and the ester, after distillation, treated with bromine in ethereal solution at -10° to -5°. The percentage yield of bromide (polybromide number) and its bromine content re determined. The methyl ester, b. p. 195—240°/15 mm., has polybromide number 38.3, Br 68.31%, calc. for methyl elupanodonele, Br 68.79%; ethyl ester, (1), b. p. 195—240°/15 mm., (2) b. p.

240—265°/15 mm., has polybromide number (1) 32.5, 33.8, (2) 85.4 (? 35.4), Br (1) 67.43, 67.48%, (2) 69.49%, calc. for ethyl clupanodionate, Br 67.84%; *n*-butyl ester, b. p. 190—245°/15 mm., has polybromide number 31.5, Br 67.64%, calc. for butyl clupanodionate, Br 65.82%. That substitution does not occur is probable, since the *n*-butyl ester from linseed oil, b. p. 190—240°/15 mm., gives a bromide, m. p. 160° (polybromide number, 51.0), Br 59.30%, evidently *n*-butyl hexabromostearate, for which Br 59.38%. Debromination of the bromide of the lower boiling ethyl ester of menhaden oil, by means of zinc and alcohol, gives an ester, iodine number 333, from which an acid, iodine number 342, mol. wt. 305, is obtained on hydrolysis. It is therefore evident that a pure ester of clupanodonic acid,  $C_{18}H_{28}O_2$ , is not obtained in this way (cf. Tsujimoto, A., 1921, i, 78). Analytical data are given to show that the methyl ester of menhaden oil may be partly separated by distillation into fractions, varying in boiling point between 156—166°/15 mm. and 255—260°/15 mm., which are probably derived from acids of the  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$ ,  $C_{20}$ , and  $C_{22}$  series. Treatment of the lead soaps of menhaden oil by means of ether, and decomposition of the separated portions, give solid and liquid acids, but the methyl esters derived from the latter are also only partly separable by distillation. Separation of the barium soaps by means of benzene containing moist alcohol gives a liquid mixture of acids, of molecular weight varying between 255.2 and 336.7, from which methyl esters are obtained, probably containing methyl arachidonate, methyl docosapentenoate, and perhaps methyl docosahexenoate. The most complete separation is effected by reducing the polybromides by means of zinc and methyl alcohol, and fractionally distilling the product. A fraction is obtained which is believed to be pure methyl clupanodionate, b. p. 215°/15 mm.,  $n_D^{20}$  1.4860, iodine number 348.8. The corresponding bromide, methyl octobromostearate, is a white, amorphous solid, m. p. 240°. In other fractions, the presence of methyl arachidonate, methyl eicosapentenoate, methyl docosatetrenoate, methyl docosapentenoate, and methyl docosahexenoate seems probable. Exactly similar results are obtained starting from cod oil or herring oil.

Unsaturated acids are obtained by the hydrolysis of the unsaturated esters derived from the polybromides. These are brominated, giving liquid and solid bromides, which are separately reduced, and again brominated. By suitable analyses, made at each step, it is shown that the liquid bromides contain less bromine than the solid bromides, and that, on reduction, the former give a product having an iodine number lower than that of the original acid, whilst the molecular weight is only slightly less. This product, on re bromination, yields only a small amount of solid bromides. Since the degree of unsaturation decreases, structural change evidently occurs. Probably either a double bond migrates to the  $\alpha\beta$ -position in respect to the carboxyl (or ester) group, or a double bond may disappear by ring formation, as from a 1:5-diene grouping.

The following analytical data are recorded. Menhaden oil has saponification number, iodine number, and  $n_D^{20}$ , respectively, 191.2,

51.7, 1.4778. Salmon oil has 185.0, 137.2, 1.4768. Cod oil has 86.9, 151.0, 1.4770. Herring oil has 186.5, 139.8, 1.4765. Sardine oil has 187.3, 158.1, 1.4791. W. S. N.

**Sludge Formation in Transformer Oils.** HANS STÄGER *Helv. Chim. Acta*, 1923, 6, 386—396).—When the type of oil used in transformers is extracted with acetone, the portion removed consists principally of unsaturated cyclic compounds. The residual oil, however, still gives the normal decomposition products when subjected to prolonged heating in air, namely, acids soluble in oil, and soluble and insoluble sludges containing asphaltic acids and asphalt-like products. The acetone-soluble portion is not, therefore, solely responsible for the sludge formation. [Cf. *J.S.C.I.*, 1923, July.] E. H. R.

**Reduction of Ethyl Ethylidenemalonate as Affected by Choice of Reducing Agent.** LUCY HIGGINBOTHAM and ARTHUR APFORTH (T., 1923, 123, 1618—1624).

[Physical] **Properties of Sodium Potassium Tartrate Tetrahydrate Related to the Piezo-electric Effect.** JOSEPH VALASEK *Physical Rev.*, 1922, 20, 639—664; cf. *ibid.*, 1922, 19, 478; 1921, [7, 475].—In an investigation of the nature of the structure underlying piezo-electric phenomena, a study was made of the temperature-variation between  $-30^\circ$  and  $+30^\circ$  of various physical properties of sodium potassium tartrate tetrahydrate. From results of the measurement of the refractive index, the following are abstracted: for the barium line  $\lambda$  5536,  $n^{21.3} = 1.49170$ , 1.49348, and 1.49721 for the  $\alpha$ ,  $\beta$ , and  $\gamma$  axes, respectively, of the index ellipsoid, these having the same direction as the  $c$ ,  $b$ , and  $a$  crystallographic axes. Corresponding values for  $n^0$  are 1.4930, 1.4947, and 1.4986, respectively. The variation with temperature is linear, the average coefficient being  $59 \times 10^{-6}$  per  $1^\circ$ . The coefficient of volume expansion was found to be 0.0001428, and since the substance has  $d^0$  1.766,  $d'$  1.766—0.0002522 $t$  between  $-10^\circ$  and  $+20^\circ$ . The specific rotatory power of an aqueous solution changes less than  $0.4^\circ$  between  $4^\circ$  and  $40^\circ$ ;  $[\alpha]_D^{25} + 25.9^\circ$ . The electrical conductivity depends between  $-20^\circ$  and  $+30^\circ$  on the direction of the current; above  $20^\circ$ , it increases very rapidly. The following values are abstracted:  $-65^\circ$ ,  $2.0 \times 10^{-14}$  mhos/cm.<sup>3</sup>;  $0^\circ$ ,  $+9.0 \times 10^{-14}$  and  $-5.0 \times 10^{-14}$ ;  $20^\circ$ ,  $+22.0 \times 10^{-14}$  and  $-11.0 \times 10^{-14}$ ;  $43^\circ$ ,  $500 \times 10^{-9}$ . Values for the electro-optic constant,  $e_{41}$ , were computed; that at  $20^\circ$  is  $-1.94 \times 10^{-8}$ , and a real pyro-electric effect was unexpectedly observed. The ultra-red absorption band is computed to be at about  $55 \mu$ . Rochelle salt appears to be an exception to Neumann's principle of symmetry. A. A. E.

**Synthesis of Glycuronic Acid from Dextrose.** MAX BERGMANN and W. WALTER WOLFF (*Ber.*, 1923, 56, [B], 1060—1065).—An example is given of the production of a reducing acid of the sugar group by the oxidation of a glucoside.

$\alpha$ -Methylglycuronic acid,  $2C_6H_{12}O_7 \cdot H_2O$ , flat, prismatic plates, m. p.  $130^\circ$ , to a viscous liquid which decomposes at about  $140^\circ$ ,

$aa^*$

$[\alpha]_D^{25} + 51.9^\circ$  in absolute alcohol, is prepared by the action of bromine and aqueous sodium hydroxide on a solution of  $\alpha$ -menthylglucoside (Fischer and Bergmann, A., 1917, i, 468) in pyridine at the atmospheric temperature; the sodium, silver, barium, calcium, and lead salts are described. The acid or the corresponding  $\beta$ -menthylglycuronic acid is hydrolysed by boiling  $N/2$  aqueous hydrochloric acid, the liberated menthol is removed with ether and, after addition of sodium acetate, the solution is treated with the requisite nitrogenous base dissolved in ether, and ethyl acetate or similar solvent whereby the following compounds are produced: the phenylbenzylhydrazone of glycurolactone,  $C_{19}H_{20}O_5N_2$ , microscopic needles, m. p.  $155^\circ$ , decomp.  $158^\circ$ ,  $[\alpha]_D^{25} - 25.75^\circ$  in methyl-alcoholic solution, which is converted by alkalis into the salts and by alcoholic ammonia into the amide (quadratic leaflets, m. p.  $176^\circ$ ) of the corresponding acid; the phenylhydrazide of glycuronic acid phenylhydrazone,  $C_{18}H_{22}O_5N_4$ , m. p.  $182^\circ$ , decomp.  $185^\circ$ ; the aniline compound,  $(C_{12}H_{14}O_5NNa)_2 \cdot H_2O$ , m. p.  $212^\circ$ . ( $\beta$ -Menthylglycuronic acid and aniline give a compound,  $C_{38}H_{63}O_{14}N$ , hexagonal plates, m. p.  $182^\circ$ .)

$\alpha$ -Methylglucoside is converted by barium hydroxide and bromine in aqueous solution at the atmospheric temperature into glyoxylic acid which was identified as the phenylbenzylhydrazone, colourless needles, m. p.  $172^\circ$ , and the phenylmethylhydrazone, large, colourless leaflets, m. p.  $170^\circ$ .

H. W.

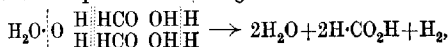
**Lysocleithins and Lysocephalins.** P. A. LEVENE and Ida P. ROLF (*J. Biol. Chem.*, 1923, 55, 743-749).—It has been shown that by the action of cobra venom on egg-yolk the unsaturated fatty acid radicles are removed from the lecithin therein contained with the production of a phosphatide to which the name lysolecithin has been given (cf. Delezenne and Fournau, A., 1914, i, 781). A reinvestigation of this action has shown that the cephalin contained in the egg-yolk undergoes a similar transformation. Thus, hydrolysis of the phosphatide fraction from the product of the action of cobra venom on eggs yielded palmitic and stearic acids, choline, and hydroxyethylamine; no unsaturated acids were, however, present. It is proposed to use the names *lysolecithin* and *lysocephalin* for the partly hydrolysed phosphatides produced by the action of cobra venom on lecithin and cephalin, respectively. Since several lecithins, differing in the nature of their saturated fatty acids, are known to occur, it is probable that several lysolecithins also exist. So far, it has been impossible to effect a separation of lysolecithin and lysocephalin by means of their cadmium chloride compounds.

E. S.

**The Mechanism of Oxidative Processes. V. Oxidation of Aldehydes.** HEINRICH WIELAND and AUGUST WINGLAS (*Annalen*, 1923, 431, 301-322; cf. A., 1921, i, 889).—Formaldehyde reacts in aqueous or ethereal solution with hydrogen peroxide, with formation of dihydroxymethyl peroxide,  $OH \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot OH$ , large, glistening prisms, m. p.  $62-64^\circ$  (slight decomp.), which is identical with the impure product described by Legler (*Annalen*,

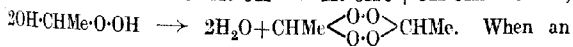
883, 217, 381) as hexa-oxyethylene-triperoxide. The compound decomposes when warmed, either alone or in solution, with production of two molecules of formic acid and one molecule of hydrogen. The reaction proceeds in non-hydroxylic solvents, but is catalysed by hydroxyl-ions. The hydrogen evolved is non-reactive; iodine is not decolorised when added to the solution containing the decomposing peroxide, and neither methylene-blue nor benzoquinone is reduced. If, however, the reaction is conducted in the presence of alladium black, formaldehyde is produced, because the hydrogen formed is sufficiently activated by the catalyst to react in the sense of the equation:  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{2\text{H}} 2\text{CH}_2(\text{OH})_2$ . On account of the instability of the oxygen-oxygen linking, the peroxide is a somewhat vigorous oxidising (dehydrogenating) agent. Iodine is rapidly liberated from iodides, sulphurous acid is oxidised to sulphuric acid, and quinol to quinone. In each of these reactions, if the aqueous solution is warmed with zinc dust, formaldehyde is produced. When the dry peroxide decomposes, or when the decomposition takes place in neutral aqueous solution, an excess of formic acid (compared to hydrogen) is obtained, owing to the side-reaction:  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{H}\cdot\text{CO}_2\text{H} + \text{H}\cdot\text{CHO} + \text{H}_2\text{O}$ , the mechanism suggested being:  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{H}\cdot\text{CHO} + \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{OH}$ ;  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{OH} \rightarrow \text{H}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$ . The heat of formation of the peroxide (75 Cal.) may be computed from the heat of formation of formic acid from formaldehyde and oxygen ( $2 \times 61$  Cal.), and the heat of decomposition of hydrogen peroxide ( $-47$  Cal.).

The conclusion of Bach and Generosow (this vol., i, 13), that the reaction between hydrogen peroxide and formaldehyde in alkaline solution proceeds according to the scheme:



is severely criticised, particularly in view of the decomposition of dihydroxymethyl peroxide in the absence of water, the a priori unlikelihood that water would undergo fission in the manner suggested, and the inactivity of the hydrogen evolved.

Acetaldehyde also gives a peroxide, but the reaction is reversible,  $2\text{Me}\cdot\text{CHO} + \text{H}_2\text{O}_2 \rightleftharpoons \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH}$ , since an aqueous solution containing acetaldehyde (2 mols.) and hydrogen peroxide (1 mol.) gives the reactions of both constituents even after standing. *Dihydroxyethyl peroxide* is obtained from the ethereal solution as a colourless oil, having a faint pungent odour, somewhat reminiscent of paraacetaldehyde, and possessing properties very similar to those of the lower homologue (cf. Baeyer and Villiger, A., 1900, i, 626). The action of mineral acids causes decomposition into acetaldehyde and hydrogen peroxide. On keeping under reduced pressure, more rapidly on warming, acetaldehyde and water are eliminated, with formation of diethylidene diperoxide, an insoluble, very explosive resin:  $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{Me}\cdot\text{CHO} + \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH}$ ;



aqueous solution of dihydroxyethyl peroxide is warmed (cf. Heimrod and Levene, A., 1911, i, 13), hydrogen is not evolved, but decomposition occurs in two directions with formation of (1) acetaldehyde (2 mols.) and hydrogen peroxide (1 mol.), or (2) aldehyde, acetic acid, and water. The latter reaction evidently proceeds as follows:  $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH} + \text{Me}\cdot\text{CHO}$ ;  $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{Me}\cdot\text{CO}_2\text{H}$ , and is analogous to the side-reaction in the decomposition of dihydroxymethyl peroxide. In the presence of an excess of concentrated sodium hydroxide the fission into acetaldehyde and hydrogen peroxide is quantitative. The behaviour of this peroxide is thus, in contrast to the lower homologue, similar to that of the chloral derivative,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{O}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$  (Baeyer and Villiger, *loc. cit.*), and the analogous product from benzaldehyde and hydrogen peroxide (Nef, A., 1898, i, 102). Hydrogen is, however, eliminated at low temperatures in the presence of silver or palladium black.

Many views have been expressed concerning the constitution of the oily residue, which is left from the distillation of ethyl ether which has been kept for some time, and has oxidising properties (cf. Clover, A., 1922, i, 619). It is now shown to be identical with dihydroxyethyl peroxide. The first stage in its formation may be dehydrogenation, with production of hydrogen peroxide:  $\text{Et}_3\text{O} + \text{O}_2 \rightarrow \text{Et}\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_2 + \text{HO}\cdot\text{OH}$ . The vinyl ether so formed would then undergo hydrolytic fission into alcohol and acetaldehyde, the latter then reacting with the hydrogen peroxide.

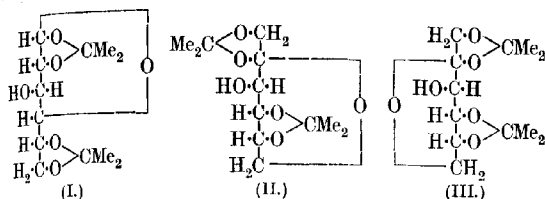
It is regarded as probable that dihydroxymethyl peroxide is an intermediate stage in the production of formic acid by the electrolysis of aqueous formaldehyde solution (Müller, A., 1920, i, 709), or by the action of metallic oxides, whilst the formation of acetic acid from acetaldehyde by the action of silver oxide in alkaline solution proceeds in an analogous manner. W. S. N.

**Optical Rotations of the Sugars. II. The Methyl Pentoses and the Glucosides.** JOHN GWILLIAM MALTBY (T., 1923, 123, 1404—1409).

**The Structure of the Normal Monosaccharides. I. Xylose.** EDMUND LANGLEY HIRST and CLIFFORD BURROUGH PURVES (T., 1923, 123, 1352—1360).

**Acetone Sugars. III. The Constitution of the Diacetone [Disopropylidene] Compounds of Dextrose and Lævulose.** KARL FREUDENBERG and ARNOLD DOSER (*Ber.*, 1923, 56, [B], 1243—1247).—Toluene-*p*-sulphonyldextrosediacetone (Freudenberg and Ivers, A., 1922, i, 523) is slowly converted by boiling hydrazine into hydrazinodiacetoneglucose (Freudenberg and Brauns, A., 1922, i, 1117). The latter compound is converted by cold, concentrated hydrochloric acid into trihydroxypropylpyrazole hydrochloride,  $\text{OH}\cdot\text{CH}_2[\text{CH}(\text{OH})]_2\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{CH} \end{smallmatrix} \text{HCl}$ , m. p.  $139^\circ$  (corr.),  $[\alpha]_{\text{D}}^{20} +5.6^\circ$  in aqueous solution. The constitution of the salt is deduced from the observation that it is oxidised by potassium permanganate

to pyrazole-3-carboxylic acid, m. p. 215° (corr.). It follows therefore that the hydroxy-group in position 3 of diacetoneglucose is unsubstituted. The constitution shown in formula I is therefore assigned to diacetonedextrose [dextrose diisopropylidene ether]; it is regarded as definitely established as far as the upper half is concerned, and very probable with regard to the lower half. The constitutions II and III are assigned to the two diacetonelævuloses.

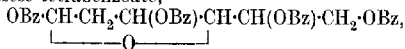


H. W.

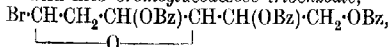
**Unsaturated Reduction Products of the Sugars and their Transformations. V. 2-Deoxyglucose (Glucodesose). II.** MAX BERGMANN, HERBERT SCHOTTE, and WOLFGANG LESCHINSKY (*Ber.*, 1923, **56**, [B], 1052—1059).—A fuller account of 2-deoxyglucose and its derivatives (cf. A., 1922, i, 227).

$\beta$ -2-Deoxyglucose has  $[\alpha]_D^{18} +15.03^\circ$  in pyridine after the solution has been prepared for five minutes and  $[\alpha]_D^{20} +90.21^\circ$  after twenty-four hours.  $\alpha$ -2-Deoxyglucose has  $[\alpha]_D^{19} +90.11^\circ$  in pyridine after five minutes. The mutarotation of the  $\beta$ -variety in pyridine is greatly affected by the presence of water or, particularly, of methyl alcohol. In aqueous solution, either form has  $[\alpha]_D +46.6^\circ$ ; since mutarotation cannot be observed, it appears that the change proceeds so rapidly that it is complete before polarimetric readings can be taken. Crystals of either form can be obtained at will by concentrating the aqueous solutions and seeding with the desired variety if care is taken to exclude accidental seeding from the atmosphere.

Glucodesose tetrabenzoate,



m. p. 148—149° (corr.),  $[\alpha]_D^{16} +8.96^\circ$  in tetrachloroethane, has been isolated in the homogeneous condition by the action of benzoyl chloride on  $\alpha$ -glucodesose in the presence of pyridine and chloroform. It is converted by hydrogen bromide in the presence of glacial acetic acid into *bromoglucodesose tribenzoate*,



long needles or broad hexagonal plates, m. p. 139° (corr.) when rapidly heated,  $[\alpha]_D^{19} +121.4^\circ$  when dissolved in tetrachloroethane, which is transformed by silver carbonate in the presence of moist acetone into *glucodesose tribenzoate*, long needles, m. p. 123° (corr.),  $[\alpha]_D^{19} +38.39^\circ$  in tetrachloroethane. *Deoxymethylglucoside tribenzoate*, m. p. 88°,  $[\alpha]_D^{19} -34.31^\circ$  in tetrachloroethane, is prepared

by treating the bromo-derivative with an excess of dry silver carbonate and anhydrous methyl alcohol; dibenzoylation by means of alcoholic ammonia and subsequent acetylation of the product of the reaction leads to the isolation of  $\beta$ -2-deoxymethylglucoside triacetate, m. p. 96—97°,  $[\alpha]_D -30.3^\circ$  when dissolved in tetrachloroethane.

Reduction of 2-deoxyglucose by sodium amalgam in as neutral as possible solution yields 2-deoxysorbitol [2-deoxymannitol],  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , prisms, m. p. 105—106° to a turbid liquid after softening at 104°,  $[\alpha]_D^{20} +15.61^\circ$  in aqueous solution. It does not exhibit the reactions characteristic of deoxy-sugars. The corresponding *diisopropylidene ether*,  $\text{C}_{12}\text{H}_{22}\text{O}_5$ , is a syrupy liquid which distils at 120—125°/1 mm. (temperature of bath),  $[\alpha]_D^{20} +11.08^\circ$  in tetrachloroethane.

*Deoxygluconic acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is prepared by oxidising 2-deoxyglucose with bromine in aqueous solution at the atmospheric temperature; it has m. p. 146—147° (corr.) after previous softening,  $[\alpha]_D^{20} +4.30^\circ$  in aqueous solution which becomes constant at +10.85° after twenty-four hours. When heated in a high vacuum at 100°, it appears partly to sublime and to pass into the corresponding *lactone*,  $\text{C}_6\text{H}_{10}\text{O}_5$ . *Barium deoxygluconate*,  $(\text{C}_6\text{H}_{11}\text{O}_6)_2\text{Ba}\cdot\text{H}_2\text{O}$ ,  $[\alpha]_D^{19} +13.37^\circ$  in aqueous solution, crystallises in long prisms which are very sparingly soluble in water.

H. W.

#### A Revision of Rosanoff's Diagram of the Aldose Sugars.

J. J. WILLAMAN and CLARENCE A. MORROW (*J. Amer. Chem. Soc.*, 1923, 45, 1273—1280).—Rosanoff's diagram of the aldose sugars (*ibid.*, 1906, 28, 114) has been modified in such a way as to include (1) all the known sugars, and (2) the name of the sugar, its specific rotation, and an indication whether it occurs in nature. Also, diagrams have been constructed for the known ketoses and the methyl hexoses. For further details, the original should be consulted, as it does not lend itself to abstraction.

W. S. N.

**The Structure of Sucrose.** MAX BERGMANN (*Ber.*, 1923, 56, [B], 1227).—In connexion with the recent observations of Haworth and Linnel (*T.*, 1923, 123, 294, 301) that the presence of the ethylene oxide ring in sucrose is improbable, it is pointed out that the author has previously drawn a similar conclusion by his work on the methylcycloacetal of  $\delta$ -acetylbutyl alcohol (*cf.* A., 1922, i, 618).

H. W.

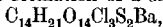
**Two New Derivatives of Trehalose and Mannitol and  $\alpha$ -Methylglucoside Dichlorohydrin.** BURCKHARDT HELFERICH, ALBRECHT LÖWA, WALDEMAR NIPPE, and HANS RIEDEL (*Ber.*, 1923, 56, [B], 1083—1087).—In a preliminary communication, the reaction between glucosides, pyridine, and sulphuryl chloride has been discussed and crystalline derivatives of  $\alpha$ - and  $\beta$ -methylglucosides have been described. Similar compounds have now been obtained from trehalose and mannitol, but not, however, from a large number of non-aldehydic sugars and sugar derivatives.

appears that the configuration present in  $\alpha$ -methylglucoside is essential for the production of these derivatives.

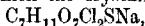
*Mannitol tetrachlorohydrin sulphate*,  $C_6H_8O_4Cl_4S$ , is prepared by the addition of a suspension of finely-divided mannitol in chloroform to a mixture of pyridine, chloroform, and sulphuryl chloride; it crystallises in leaflets, m. p.  $107^\circ$ ,  $[\alpha]_D^{25} +105.13^\circ$  when dissolved in tetrachloroethane.

*Trehalose tetrachlorohydrin disulphate*,  $C_{12}H_{14}O_{11}Cl_4S_2$ , colourless, lustrous needles which become carbonised at about  $175^\circ$ , is prepared in a similar manner; it has  $[\alpha]_D^{27} +151.9^\circ$ ,  $[\alpha]_D^{20} +152.29^\circ$  when dissolved in chloroform.

$\alpha$ -Methylglucoside dichlorohydrin sulphate, for which an improved method of preparation is given, has been examined in greater detail. It is slowly hydrolysed by aqueous barium hydroxide solution at  $37^\circ$  with the formation of a barium salt,



an amorphous, white precipitate, of which the homogeneity appears somewhat doubtful. Methyl-alcoholic ammonia transforms it into the amorphous ammonium salt of an  $\alpha$ -methylglucoside dichlorohydrin sulphate, from which the crystalline sodium salt,



broad needles, copper salt,  $(C_7H_{11}O_7Cl_2S_2)_2Cu \cdot 3.5H_2O$ , blue, rhombic leaflets,  $[\alpha] +123.87^\circ$  to  $+125.56^\circ$  in aqueous solution, and the amorphous barium salt (which is not identical with the salt described above) are derived. The sodium salt is converted when in boiling aqueous solution in the presence of an excess of copper sulphate into  $\alpha$ -methylglucoside dichlorohydrin,  $C_7H_{12}O_4Cl_2$ , colourless needles, m. p.  $155^\circ$ ,  $[\alpha]_D^{20} +180.7^\circ$  in alcoholic solution. H. W.

**Hydrolysis of Starch by Salts. II.** W. BIEDERMANN (*Biochem. Z.*, 1923, 137, 35—52).—A few experiments are described where a comparison is made of the colour produced by iodine on various dilutions of (1) an amylose solution mixed with a phosphate mixture and shaken continuously in a stream of air, (2) an unshaken amylose solution mixed with a phosphate mixture, the solutions being kept a few hours before testing with iodine. Instead of phosphate mixtures,  $N/5$ -sodium and potassium chlorides were also employed. The results are interpreted as indicating hydrolysis of the amylose by the salts in presence of oxygen. A long discussion follows as to a possible explanation on a purely physical basis.

H. K.

**Polysaccharides. XX. Polymeric Carbohydrates.** P. KARRER (*Helv. Chim. Acta*, 1923, 6, 402—409).—When Zulkowsky's soluble starch is treated at  $0^\circ$  with acetyl bromide, as much acetyl-bromomaltose, and finally hepta-acetylmaltose, is obtained as from an equal quantity of maltose, and only a trace of tetra-acetylglucose is obtained. If a proportion of glucose is added to the starch, the expected yield of tetra-acetylglucose is obtained. If, as Irvine claims, starch were derived from a triamylose, by the action of acetyl bromide, it should give half as much acetyl-bromoglucose as acetyl-bromomaltose. Irvine's conclusion cannot therefore be

maintained, and Pictet's trihexosan theory also falls to the ground for similar reasons (A., 1922, 1, 987). Irvine's view that cellobiose is contained in the starch molecule is also not confirmed, since no cellobiose derivative is found among the reaction products from the action of acetyl bromide. Irvine's methylation process by which he obtained 2:3:6-trimethylglucose is too drastic and cannot be trusted for the determination of constitution. The fact that by the methylation of inulin sometimes dextrorotatory and sometimes levorotatory products are obtained shows that methylation may lead to decomposition. The remainder of the paper is a polemical reply to Irvine (T., 1922, 121, 1060, 1213).

E. H. R.

**Soluble Starch or Amylodextrin.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1923, 32, 221—227).—The author reviews the processes previously described for the preparation of soluble starch both by means of hydrolysing and oxidising reagents, and describes a new procedure whereby a preparation can be obtained which gives a very stable and limpid solution. One hundred parts of starch are digested for about twenty hours with 130—150 parts of a 0.75% solution of potassium dichromate in *N*/4-hydrochloric acid, the dichromate is then reduced with a trace of sulphur dioxide, and the product is collected by filtration, washed, and dried at a low temperature. Potassium permanganate may be substituted for the dichromate, if desired. The starch oxidised in this way swells, but does not dissolve in boiling water, but on the addition of a trace of alkali hydroxide, or even of ammonia or alkali carbonate, the mucilage is rapidly transformed into a limpid solution absolutely free from microscopic particles. The soluble starch solution has all the properties usually attributed to amylodextrin, and is not precipitated by acidification. It has but little reducing action on Fehling's solution, and is strongly dextrorotatory,  $[\alpha]_D$  about  $+200^\circ$ .

G. F. M.

**The Composition of Glycogen.** M. SAMEC and V. ISAJEVIĆ (*Compt. rend.*, 1923, 176, 1419—1421).—A comparison of the physico-chemical properties of glycogen with those of starch shows that the molecular weights are of the same order. On submitting solutions of the two substances to electro-dialysis similar phenomena are observed, the chief difference being that a starch solution deposits about 80% of the solute in the form of gel, whereas a glycogen solution yields but little gel: this is consistent with the low viscosity of the latter solution. The phosphorus content of the glycogen sol is high, although its electrical conductivity is low. The authors suggest that this quantity of phosphorus is of great physiological importance, and that glycogen may function as a reserve of phosphorus in addition to one of carbohydrate.

H. J. E.

**Some Physico-chemical Properties of Laminarin.** (MNE) L. GRUZEWSKA (*Bull. Soc. Chim. biol.*, 1923, 5, 216—226).—Laminarin (cf. Kylin, A., 1915, 1, 931) forms a colloidal solution in water which is unstable and slowly deposits the substance in

the form of grains. The author regards this spontaneous precipitation as the result of polymerisation or condensation. The presence of oxygen appears to be necessary for its production; it is also accelerated by acids and by hydrogen peroxide and retarded by alkalis. Although laminarin forms colloidal solutions it diffuses slowly through a collodion membrane, and hence cannot be purified by dialysis. Crystalline deposits have been obtained from alkaline solutions of laminarin after the addition of alcohol and ether.

E. S.

**Hydrocellulose.** EMIL HEUSER and GEORG JAYME (*Ber.*, 1923, 56, [B], 1242—1243; cf. Heuser and von Neuenstein, this vol., i, 17).—The molecular weight of dimethylhydrocellulose has been determined cryoscopically in aqueous solution. The results are in harmony with the authors' conception that the compound is a dimethyl derivative of a dimeric anhydrocellobiose, which receives further confirmation from the observation that the molecular weight does not increase beyond the theoretically required value with increasing concentration of the solution.

H. W.

**Hydrocellulose. II. Hydrolysis of Cellulose by Oxalic Acid.** EMIL HEUSER and FRITZ EISENRING (*Cellulosechemie*, 1923, 4, 25—31).—In the preparation of hydrocellulose from viscose cellulose by the action of hydrogen chloride gas in the presence of limited quantities of moisture according to the method of Knoevenagel and Busch (*A.*, 1922, i, 636), the attack on the cellulose is more severe and the yield of product reprecipitable from its solution in 8% sodium hydroxide solution is lower the greater the quantity of moisture present during the action of the hydrogen chloride. By secondary hydrolysis of the hydrocellulose with dilute sulphuric acid, the quantity of dextrose formed is also larger when more moisture is present. The composition of the product reprecipitated by alcohol from solutions of the viscose hydrocellulose in alkali hydroxide corresponds with a compound of the formula  $C_{12}H_{20}O_{10} \cdot 2NaOH$ . Viscose hydrocellulose, when submitted to total hydrolysis with 41% hydrochloric acid for twenty-eight hours at 18—20°, yielded more than 95% of fermentable dextrose. Hydrocellulose completely soluble in alkali hydroxide solution is produced by digesting viscose cellulose with 10—20% oxalic acid solution in a sealed tube at 100° without serious loss in the form of soluble products. With 5% oxalic acid solution at higher temperatures (140—180°), considerable quantities of reducing sugar are formed, depending on the time and temperature, and the yield of hydrocellulose residue is correspondingly reduced. At 180°, large quantities of gaseous products are formed owing to the decomposition of the oxalic acid. Ordinary cotton cellulose when heated with oxalic acid yields a hydrocellulose which is only partly soluble in 10% sodium hydroxide solution. When digested with oxalic acid solution at 180°, viscose hydrocellulose yields large proportions of *o*-hydroxymethylfurfuraldehyde, viscose cellulose yields much less, and cotton cellulose only a small quantity [Cf. *J.S.C.I.*, 1923, July].

J. F. B.

**Derivatives of Straw-lignin. II.** F. PASCHKE (*Cellulosechemie*, 1923, 4, 31—32).—When heated at  $180^\circ$  with aniline and oxalic acid, straw-lignin forms a condensation product in which 1 mol. of lignin is combined with 3 mols. of aniline. When straw-lignin is fused with sulphur and sodium sulphide, a sulphur dye is formed having a composition corresponding with the formula  $C_{36}H_{40}O_{21}S_8$ . This points to the presence of four methoxyl groups in the lignin molecule, and probably also of four hydroxyl groups. In its condensation reactions, lignin exercises trivalent aldehydic or ketonic functions, and the presence of six sulphur atoms in the above formula falls in the same category. In faintly alkaline solution, straw-lignin and wood-lignin prepared by the alkaline process of digestion have a tanning action on animal skin, which after twenty-four hours' immersion in the solution is converted into a soft brown leather without gain in weight. An alkaline solution of ligninsulphonic acid, on the other hand, has no tanning action on skin but a large proportion of the extract is absorbed. The gain in weight is considerable but the product after drying becomes extremely brittle. J. F. B.

**A Note on the Photosynthesis of Amines.** OSCAR WALTER SNOW and JOHN FREDERICK SMERDON STONE (*T.*, 1923, 123, 1509—1515).

**Double Salts of Mercuric Chloride with the Chloroplatinates of Amines.** D. STRÖMHOLM (*Z. anorg. Chem.*, 1923, 126, 129—140; cf. A., 1902, i, 138).—Mercurichlorides of compounds of the type  $(NH_2R)_4PtCl_6$  are described. Of the 27 compounds mentioned, eight contain 6 molecular proportions of mercuric chloride (which appears to be the maximum amount possible), four contain 5 molecular proportions, one contains 4.5, nine contain 4, and the rest contain less than 4 molecular proportions.

The following compounds are described:  $(NH_3)_4PtCl_6 \cdot HgCl_2$ ;

$(NH_3)_4PtCl_6 \cdot (HgCl_2)_4 \cdot 3H_2O$ ;  $(NH_2Me)_4PtCl_6 \cdot (HgCl_2)_4$ ;

$(NH_2Et)_4PtCl_6 \cdot (HgCl_2)_6$ ;  $(NH_2Pr^a)_4PtCl_6 \cdot 2H_2O$ ;

$(NH_2Pr^a)_4PtCl_6 \cdot (HgCl_2)_{2.5}$ ;  $(CH_3Pr^a \cdot NH_2)_4PtCl_6 \cdot 2H_2O$ ;

$(CH_3Pr^a \cdot NH_2)_2PtCl_6 \cdot (HgCl_2)_2$ ;  $(NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)_2PtCl_6$ ;

$(NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)_2PtCl_6 \cdot (HgCl_2)_5$ ;  $(C_2H_5 \cdot N)_4PtCl_6 \cdot (HgCl_2)_2$ ;

*cis*-( $NH_3$ )<sub>2</sub>( $NH_2Pr^a$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>4.5</sub>;

*trans*-( $NH_3$ )<sub>2</sub>( $NH_2Pr^a$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>6</sub>;

*cis*-( $NH_2Me$ )<sub>2</sub>( $NH_2Pr^a$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>3</sub>;

*trans*-( $NH_2Me$ )<sub>2</sub>( $NH_2Pr^a$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>5</sub> or <sub>6</sub>;

*cis*- and *trans*-( $NH_2Et$ )<sub>2</sub>( $NH_2Pr^a$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>4</sub>;

*cis*-( $NH_3$ )<sub>2</sub>( $CH_3Pr^a \cdot NH_2$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>3.5</sub>;

*trans*-( $NH_3$ )<sub>2</sub>( $CH_3Pr^a \cdot NH_2$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>6</sub>;

*trans*-( $NH_2Me$ )<sub>2</sub>( $CH_3Pr^a \cdot NH_2$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>5</sub>;

*trans*-( $NH_2Et$ )<sub>2</sub>( $CH_3Pr^a \cdot NH_2$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>5</sub>;

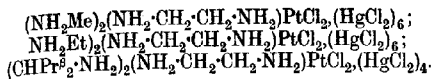
( $NH_3$ )<sub>2</sub>( $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ )PtCl<sub>6</sub>·( $HgCl_2$ )<sub>4</sub>;

*cis*- and *trans*-( $NH_3$ )<sub>2</sub>( $NH_2Me$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>4</sub>;

*cis*- and *trans*-( $NH_3$ )<sub>2</sub>( $NH_2Et$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>4</sub>;

*cis*-( $NH_2Me$ )<sub>2</sub>( $NH_2Et$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>6</sub>;

*trans*-( $NH_2Me$ )<sub>2</sub>( $NH_2Et$ )<sub>2</sub>PtCl<sub>6</sub>·( $HgCl_2$ )<sub>4</sub>;



H. H.

**A New Class of Complex Compounds of Ruthenium.** A. UTBIER (*Ber.*, 1923, 56, [B], 1008—1011; cf. Gutbier and Krauss, 1915, i, 120).—Complex ruthenium compounds of the type  $\text{RuX}_2\cdot 4\text{NH}_3\cdot \text{R}\cdot \text{X}$  are uniformly obtained when the necessary proportion of the organic base dissolved in dilute halogen acid is added very rapidly to a solution of the ruthenium halide in the presence of a sufficient amount of halogen acid; the precipitates are recrystallised from water or alcohol acidified with halogen acid. The salts are highly sensitive to pure water, so that their physico-chemical behaviour in this medium cannot be studied. The constitution as not yet been definitely elucidated, but, for the present, the author adopts Werner's conception and considers that the four molecules of the substituted ammonium halide are each united to the ruthenium atom by a subsidiary valency of the halogen atom, thus giving a kation with the co-ordination number 6; the general formula for the salts is therefore  $[\text{RuX}_2(\text{NH}_3\text{R}\cdot \text{X})_4]\text{X}$ .

The following individual salts are described: Chloro-series, the *methylammonium* salt,  $[\text{RuCl}_2(\text{NH}_2\text{MeCl})_4]\text{Cl}$ , reddish-brown, lustrous needles; the *ethylammonium* salt, reddish-brown, feathery needles or irregular plates; the *n-propylammonium* salt, small, red, lustrous needles; the *isopropylammonium* salt, brownish-red, irregular leaflets; the *n-butylammonium* salt, lustrous, brownish-red, matted needles; the *isobutylammonium* salt, reddish-brown needles; the *ethylenediammonium* salt,  $[\text{RuCl}_2(\text{C}_2\text{H}_4\text{N}_2\text{H}_6\text{Cl}_2)_2]\text{Cl}$ , very small, red, lustrous needles or brownish-red leaflets; the *propylenediammonium* salt, purplish-red, lustrous needles or leaflets; the *pyridinium* salt, small, reddish-brown needles; the *quinolinium* salt, lustrous, brownish-red leaflets. *Bromo-series*: the *methylammonium* salt,  $[\text{RuBr}_2(\text{NH}_2\text{MeBr})_4]\text{Br}$ , small, very dark leaflets; the *ethylammonium* salt, almost black leaflets; the *n-propylammonium* salt, dark, lustrous leaflets; the *isopropylammonium* salt, small, dark leaflets; the *n-butylammonium* salt, dark leaflets; the *isobutylammonium* salt, almost black leaflets; the *ethylenediammonium* salt, very dark, irregular leaflets; the *propylenediammonium* salt, black needles; the *pyridinium* salt, dark needles or leaflets; the *quinolinium* salt, very dark, thin leaflets.

H. W.

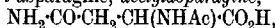
**Changes undergone by Amino-acids in Presence of Sugar.** S. KOSTYTSCHEV and W. BRILLIANT (*Z. physiol. Chem.*, 1923, 127, 224—233).—If yeast autolysate is allowed to remain with sugar at 30—55° a decrease in the amino-nitrogen takes place, and a compound which can be precipitated by copper hydroxide is formed, containing nitrogen closely corresponding in amount with that lost by the amino-acids. A spontaneous reaction between sugar and amino-acids takes place in alkaline media, with the

formation of a compound precipitable by copper hydroxide. From the precipitate the sugar, but not the amino-acids, can be recovered.

W. O. K.

**Synthesis of  $\gamma$ -Amino- $\beta$ -hydroxybutyric Acid.** MAI BERGMANN (*Z. physiol. Chem.*, 1923, **127**, 260—261).— $\gamma$ -Amino- $\beta$ -hydroxybutyric acid, synthesised by Tomita (this vol., i, 199) has also been synthesised by the author and his collaborators who have also prepared the *anhydride*, and the *hydrobromide* m. p. 78°; the *N*-benzoyl derivative, m. p. 177°; *O*-benzoyl derivative (*hydrochloride*, m. p. 215° decomp.), the isomeric benzoyl derivatives of the ester, and the amide of the acid. W. O. K.

**The Configuration of Amino-acids. I.** P. KARRER and A. SCHLOSSER (*Helv. Chim. Acta*, 1923, **6**, 411—418).—These experiments were started with the object of obtaining an optically active serine from *L*-asparagine, and although this has not yet been accomplished, a number of interesting results were obtained. By acetylation of *L*-asparagine, *acetyl*asparagine,



was obtained in 60% yield, stout prisms, m. p. 165°; a 1.5% aqueous solution is optically inactive. When treated with bromine in barium hydroxide solution, this was converted into a compound,  $\text{C}_4\text{H}_5\text{O}_3\text{N}_2$ , which was shown to be *l*-glyoxalid-2-one-5-carboxylic

acid,  $\begin{array}{c} \text{CH}_2\cdot\text{NH} \\ \text{CO}_2\text{H}\cdot\text{CH}\cdot\text{NH} \end{array} > \text{CO}$ , which forms large, rhombic crystals

[ $\alpha$ :  $b:c=0.8601:1:0.6356$ , [ $\alpha$ ]<sub>D</sub><sup>18</sup>  $-16.5^\circ$ ]; it decomposes at 184°. With diazomethane, it gives a *methyl* ester, m. p. 78°, crystallising in fine needles. It does not form salts with mineral acids, is not affected by nitrous acid, and when heated with hydrochloric acid is converted into *d*- $\beta$ - $\gamma$ -diaminopropionic acid, which was isolated as the monohydrochloride, [ $\alpha$ ]<sub>D</sub><sup>20</sup>  $+25.0^\circ$ . It follows that *L*-asparagine and *d*-diaminopropionic acid must have the same configuration as *l*-glyoxalid-2-one-5-carboxylic acid, since no change takes place at the asymmetric carbon atom. *d*-Diaminopropionic acid has previously been converted into *d*-glyceric acid (*d*-levorotatory) through *d*-isoserine, and *L*-asparagine has also been converted into *l*-glyceric acid (*d*-extro-rotatory) through *L*-aspartic acid, *L*-malic acid, and *L*-isoserine. It follows that at one of these stages a Walden inversion must occur.

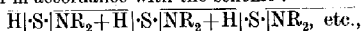
*L*-Acetyl-asparagine forms a *methyl* ester, [ $\alpha$ ]<sub>D</sub><sup>19</sup>  $-41.14^\circ$ , and an *amide* (which is the diamide of *l*-acetyl-aspartic acid) decomposing at 230°; practically it is optically inactive. E. H. R.

**The Amides of Hypothiocyanic Acid.** HANS LECHER, MAI WITTFER, and WALTER SPEER (*Ber.*, 1923, **56**, [B], 1104—1112).—The term, hypothiocyanic acid, has been applied to the compound  $\text{NCS}\cdot\text{OH}$ , by Bjerrum and Kirschner ("Die Rhodanide des Goldes und das freie Rhodan," Kopenhagen, 1918, p. 11). Attempts to prepare amides of the acid have been described by Söderbäck (*A.*, 1920, i, 219), who however, did not obtain products which could be purified. A slight modification of his procedure, however,

ich consists in adding the solution of thiocyanogen to that of excess of ammonia or amine, leads to the desired result. The *thylamide*,  $\text{NCS}\cdot\text{N}\text{Et}_2$ , is thus obtained as a colourless liquid with pleasant odour, b. p.  $37^\circ$  (corr.)/3 mm.; it is unstable at the atmospheric temperature. The *amide*,  $\text{NCS}\cdot\text{NH}_2$ , can be prepared similarly in ethereal solution which is relatively stable. It remains a colourless liquid with an odour of formaldehyde when the solvent is removed at a low temperature in a high vacuum. It is not possible to purify it, since it explodes spontaneously at  $0^\circ$  and a lower temperature has not a sufficiently high vapour tension to permit its distillation in a high vacuum.

Hydrolysis of the amides by acids results in the immediate reduction mainly of ammonium or amine salt and hypothiocyanylic acid:  $\text{NCS}\cdot\text{NR}_2 + \text{H}_2\text{O} + \text{HX} = \text{NCS}\cdot\text{OH} + \text{NHR}_2\cdot\text{HX}$ . Subsequently, hypothiocyanylic acid yields thiocyanylic acid, sulphuric acid, and hydrocyanic acid, but a portion of it is decomposed in a different reaction, since the amounts of the two latter acids which are formed are less than the theoretical. Similar observations are recorded in the case of the hydrolysis of thiocyanogen by water; the process therefore does not occur quantitatively in accordance with Söderbäck's equation:  $3(\text{SCN})_2 + 4\text{H}_2\text{O} \rightarrow 5\text{HSCN} + \text{H}_2\text{SO}_4 + \text{CN}$ .

Diethylrhodanamine is relatively stable towards water and aqueous ammonia. It is decomposed more slowly by solutions of alkali hydroxides than by acids. Hydrolysis occurs in a completely different manner, and gives cyanate, sulphur, and amine in such quantities that the main change must follow the course:  $\text{NC}\cdot\text{S}\cdot\text{NR}_2 + \text{OH} \rightarrow \text{NC}\cdot\text{OK} + \text{S} + \text{NHR}_2$ . Apparently the first phase of the reaction consists in the rupture of the bond between the sulphur and carbon atoms:  $\text{NC}\cdot\text{S}\cdot\text{NR}_2 + \text{KOH} \rightarrow \text{NC}\cdot\text{OK} + \text{HS}\cdot\text{NR}_2$ . Diethylthiohydroxylamine is thereby formed, which is either decomposed further in accordance with the scheme:



it is hydrolysed to  $\text{HS}\cdot\text{OH}$ , which yields water and sulphur.

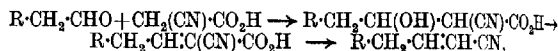
Rhodanamine is decomposed in fundamentally the same manner when its ethereal solution is shaken with alkali hydroxide solution. The bulk of the sulphur is obtained, however, in the form of polysulphide and thiosulphate. In the presence of an organic solvent such as ether, which preserves the sulphur in the molecular-disperse condition, the element appears to react readily with alkali hydroxide.

The acid hydrolysis of rhodanamine appears to proceed in part according to the scheme given for the alkaline hydrolysis, since the formation of carbon dioxide and an excess of ammonium salt points to a primary production of cyanic acid. H. W.

**Nitriles of Olefine Monocarboxylic Acids.** K. VON AUWERS (with O. JORDAN, TH. MEISSNER, and O. SEYDEL) [*Ber.*, 1923, 56, (B), 1172—1185].—The constitution of the product obtained by the action of potassium cyanide on allyl bromide or iodide has been the subject of considerable discussion, since its mode of production causes it to be regarded as allyl cyanide,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CN}$ ,

whereas its properties indicate that it is crotononitrile,  $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CN}$ . The authors have endeavoured to apply spectrochemical methods to the elucidation of its constitution, in the expectation that allyl cyanide would be optically normal, whereas crotononitrile should exhibit optical exaltation in consequence of the conjugation of the double and treble bonds. Pure allyl cyanide is most conveniently prepared from allyl bromide and cuprous cyanide; it has  $d_4^{15}$  0.8497,  $n_D^{15}$  1.40626,  $n_D^{14.5}$  1.40868,  $n_D^{14}$  1.41511,  $n_D^{13}$  1.41996. It is characterised by the unusual ease with which it becomes isomerised to crotononitrile under the influence of alkali hydroxide, and, for this reason, the use of potassium cyanide in its preparation is inadvisable. Three specimens of crotononitrile, prepared respectively from crotonaldehyde and acetic anhydride (I and II) and from crotonamide and phosphoric oxide have been examined, with the following results. (i)  $d_4^{15}$  0.8378,  $d_4^{20}$  0.829,  $d_4^{25}$  0.8259;  $n_D^{15}$  1.42859,  $n_D^{14.5}$  1.43198,  $n_D^{14}$  1.44097,  $n_D^{13.5}$  1.44879. (ii)  $d_4^{15}$  0.8226,  $n_D^{15}$  1.41566,  $n_D^{14.5}$  1.41966,  $n_D^{14}$  1.42795,  $n_D^{13.5}$  1.43518. (iii)  $d_4^{15}$  0.8304,  $n_D^{15}$  1.42164,  $n_D^{14.5}$  1.42488,  $n_D^{14}$  1.43361,  $n_D^{13.5}$  1.44103. The expected difference in the spectroscopic behaviour is therefore observed. The differences appear to be shown quite generally between  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -nitriles.

The action between aldehydes and cyanoacetic acid has been examined. The expectation that it would proceed in accordance with the scheme :

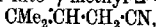


is fulfilled as far as the production of the nitrile-acid is concerned, but it is found that when the latter is decomposed with loss of carbon dioxide a displacement of the double bond occurs in such a manner that a conjugated passes into a non-conjugated system. The  $\Delta^{\beta}$ -nitrile is therefore the final product, the formation of which is not due to isomerisation of primarily formed  $\Delta^{\alpha}$ -nitrile, since the latter is stable under the experimental conditions adopted.

The following nitrile acids are obtained by the condensation of cyanoacetic acid with the requisite aldehyde in the presence of piperidine at 60—70°. They are converted into nitriles by heating them until evolution of carbon dioxide ceases; the yields are uniformly very poor, since the bulk of the material becomes resinified.

$\alpha$ -Cyanoacrotic acid, thin leaflets, m. p. 80°, yields an ethyl ester, a colourless liquid, b. p. 112°/20 mm.,  $d_4^{15}$  1.0255,  $d_4^{20}$  1.024,  $n_D^{15}$  1.44088,  $n_D^{14.5}$  1.45302,  $n_D^{14}$  1.46172,  $n_D^{13.5}$  1.46888,  $n_D^{13}$  1.4525; the nitrile obtained from it is a mixture of much crotononitrile and little vinylacetone. Propaldehyde and cyanoacetic acid yield  $\alpha$ -cyano- $\Delta^{\alpha}$ -pentenoic acid, coarse, lustrous needles, m. p. 82—84° (ethyl ester, a colourless liquid, b. p. 121—122°/25 mm.,  $d_4^{15}$  1.0004,  $d_4^{20}$  1.000,  $n_D^{15}$  1.44988,  $n_D^{14.5}$  1.45292,  $n_D^{14}$  1.46152,  $n_D^{13.5}$  1.46869,  $n_D^{13}$  1.4529) which is converted by heat into  $\Delta^{\beta}$ -penteno-nitrile, b. p. 85—87°/10 mm.,  $d_4^{15}$  0.8430,  $d_4^{20}$  0.842,  $n_D^{15}$  1.42391,  $n_D^{14.5}$  1.42650,  $n_D^{14}$  1.43374,  $n_D^{13.5}$  1.43968,  $n_D^{13}$  1.4260. isoButal-

ide and cyanoacetic acid give a small yield of the corresponding acid which is converted into  $\gamma$ -methyl- $\Delta^6$ -pentenenitrile,



colourless liquid, b. p.  $63^\circ/14$  mm.,  $d_4^{188}$  0.8556,  $d_4^{20}$  0.855,  $n_D^{188}$  1.43529,  $n_D^{188}$  1.43796,  $n_D^{188}$  1.44529,  $n_D^{188}$  1.45129,  $n_D^{20}$  1.4374. *iso*-valeraldehyde and cyanoacetic acid yield  $\alpha$ -cyano- $\Delta^6$ -*iso*-heptenoic acid, m. p.  $53^\circ$ ,  $d_4^{100}$  0.9711, whence  $d_4^{99.6}$  0.9715,  $n_D^{99.6}$  1.44367,  $n_D^{99.6}$  1.44690,  $n_D^{99.6}$  1.45599,  $n_D^{99.6}$  1.46409, which is converted by ozone into a mixture of *iso*valeraldehyde and a little *isobutaldehyde*. The corresponding *ethyl* ester is a colourless liquid of agreeable odour, b. p.  $121$ — $122^\circ/13$  mm.,  $d_4^{197}$  0.9666,  $d_4^{20}$  0.966,  $n_D^{197}$  1.45198,  $n_D^{197}$  1.45502,  $n_D^{197}$  1.46340,  $n_D^{197}$  1.47037,  $n_D^{20}$  1.4549.  $\Delta^6$ -*iso*-heptenenitrile, obtained from the  $\alpha$ -cyano-acid, has b. p.  $57$ — $88^\circ/1$  mm.,  $d_4^{22.3}$  0.8241,  $d_4^{20}$  0.826,  $n_D^{22.3}$  1.42691,  $n_D^{22.3}$  1.42932,  $n_D^{22.3}$  1.43614,  $n_D^{22.3}$  1.44166,  $n_D^{20}$  1.4304; its optical characteristics and its behaviour towards ozone prove it to be almost exclusively the  $\alpha$ -derivative. It is converted by boiling potassium hydroxide solution into a mixture of  $\Delta^6$ - and  $\Delta^5$ -*iso*heptenoic acids. H. W.

[The Catalytic Reduction of Aliphatic Azines. II. Reduction of Dimethylketazine and *iso*Butyraldazine in the Presence of Glacial Acetic Acid]. K. A. TAIPALE (*Ber.*, 1923, 56, [B], 1247; cf. this vol., i, 547).—An addendum. The lack of foreign scientific literature in Russia during the last few years has caused the author to be in ignorance of the work of Lochte, Bailey, and Noyes (*A.*, 1922, i, 329; this vol., i, 26) on the hydrogenation of dimethylketazine. H. W.

A Possible Asymmetry of Aliphatic Diazo-compounds. IV. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1923, 55, 795—800).—In previous communications (*A.*, 1921, i, 233; 1922, i, 818), experiments have been described which resulted in the production of optically active diazosuccinic ester; the rotation observed, however, was extremely small. The crude diazo-ester has now been converted into bromosuccinic ester by treatment with gaseous hydrogen bromide in ethereal solution. Hydrolysis of the bromo-ester with 10% hydrochloric acid yielded a product,  $[\alpha]_D^{20} + 0.2^\circ$ , which was a mixture of bromosuccinic, chlorosuccinic, and fumaric acids. By fractional crystallisation of 800 g. of this product, a fraction was finally obtained which melted at  $176^\circ$  and had  $[\alpha]_D^{20} + 60.45^\circ$  in ethereal solution. Analysis indicated that it contained about 10% of chlorosuccinic and 90% of bromosuccinic acids. Since pure bromosuccinic acid has  $[\alpha]_D^{20} + 67.92^\circ$  and m. p.  $172^\circ$ , it is considered that the activity of the final product was due entirely to the bromosuccinic acid, and hence that the previously observed activity of preparations of diazosuccinic ester was due, not to contaminating substances, but to the diazo-ester itself. This is supported by the observation that active malic ester is not converted into active chlorosuccinic acid when treated with hydrochloric acid under the conditions used above. An explanation of the mechanism of the asymmetry will be dealt with in a later publication.

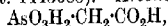
The observations of Chiles and Noyes (A., 1922, i, 924), that optically active glutamic and aspartic acids are produced by the reduction of ethyl diazoglutarate and ethyl diazosuccinate, respectively, have not been confirmed. Further, starting from *l*-asparagine, the authors have consistently obtained dextrorotatory diazosuccinic and malic esters; Chiles and Noyes, however, state that *l*-compounds are produced.

E. S.

**Preparation of Aliphatic Arsenical Compounds.** LES ÉTABLISSEMENTS POULENC FRÈRES and CARL OECHSLIN (Brit. Pat. 191029).—An arsenical aliphatic acid of the formula  $[\text{CHAs}(\text{OH})_2]_n$  is obtained by heating at  $180^\circ$ , until the evolution of carbon dioxide and acetic acid ceases, the acetylarsenious anhydride prepared by dissolving arsenious oxide in acetic anhydride. The residual mass is dried in a vacuum, reduced to a fine powder, extracted several times with sodium hydroxide or hydrochloric acid, and the insoluble, grey powder remaining, which has the composition  $(\text{AsCH}_3)_n$ , is suspended in sodium carbonate solution and oxidised with hydrogen peroxide. The resulting solution containing the sodium salt of the acid is decolorised with charcoal, and acidified with hydrochloric acid, when the acid is precipitated as a white powder, sparingly soluble in water and alcohol, but readily soluble in alkalis.

G. F. M.

**Arsonoacetic acid.** J. HUISMANN, J. CALLEN, and W. GRÜTTEFIEN (U.S. Pat. 1445685).—*Arsonosacetic acid*,



is prepared by addition of sulphuric acid to the calcium salt, the latter being obtained by interaction of arsenious oxide, chloroacetic acid, sodium hydroxide, acetic acid, ammonia and calcium chloride, successively added. It forms colourless crystals from glacial acetic acid solution, m. p.  $152^\circ$ .

CHEMICAL ABSTRACTS.

**The Action of Sulphuryl Chloride on Organic Substances.** II. THOMAS HAROLD DURRANS (T., 1923, 123, 1424—1429).

**The Walden Inversion.** A. E. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 275—288).—An explanation of the Walden inversion is given for cyclic compounds in which *cis-trans*-isomerism may exist, and the possibility of ring formation as an intermediate stage in the Walden inversion in open-chain compounds is pointed out.

R. T.

**Recent Investigations on Substitution in the Benzene Nucleus.** A. F. HOLLEMAN (*Rec. trav. chim.*, 1923, 42, 355—379).—A lecture delivered at the Universities of London and Oxford, June 7th and 9th, 1922, in which a general survey of the subject is made. No entirely satisfactory theoretical explanation of the problem of replacing a hydrogen atom in substances of the type  $\text{C}_6\text{H}_5\text{X}$  has yet been put forward. In dealing with the entry of a third substituent into a compound of the type  $\text{C}_6\text{H}_4\text{XY}$ , the quantitative aspect is also far from a satisfactory explanation, but greater progress has been made from the qualitative point of view. The replacement of substituents gives still greater scope for research,

although many substances have been prepared in this manner, the work has not been done as regards systematic replacement, and is therefore irrelevant for this purpose. A consideration of some of the more systematic investigations on comparative substitution includes references to papers by Beyer (A., 1922, i, 37), Böseken (A., 1912, i, 430), Davies (T., 1921, 119, 853, 876; 1922, 121, 785), Smroth and von Schmaedel (A., 1907, i, 620), Holleman (A., 1913, 844), Holleman and de Mooy (A., 1916, i, 22), Holleman and Inkes (A., 1911, i, 535), Holleman and Wibaut (A., 1913, i, 169), Lange (A., 1919, i, 122), Lobry de Bruyn (A., 1904, i, 388), and Wibaut (A., 1915, ii, 680).

H. J. E.

**Low Temperature Coal Tar and the Products of its Superheating.** FRANZ SCHÜTZ, WILHELM BUSCHMANN, and HEINRICH FISCHER (Ber., 1923, 56, [B], 1091—1096; cf. Schütz, this vol., i, 55).—A reply to Fischer (this vol., i, 313).

Evidence is brought forward to prove that the low temperature tar examined by the authors had not, as Fischer suggested, been subjected to superheating. The temperature (600°) cited in the original paper is that of the heating chambers, and not of the coal itself, which did not exceed 480°. The authors agree with Fischer that a temperature of 400—500° suffices for the production of low temperature tar, but do not share his view that "benzine" escapes from the coal at 300°. Tar, and simultaneously also gas, commences to be produced at 370—380° and is freely evolved at 400°. The pyrogenic decomposition of the tar-forming constituents of coal takes place within narrow limits of temperature (400—450°). With rise of temperature above 450°, the formation of tar diminishes rapidly, whereas that of gas falls more slowly. At about 500°, the change is complete in six to seven hours. The yields of the various products depend greatly on the type of coal. Ninety kg. of low temperature tar and 50 cubic metres of gas per ton were obtained from a gas coal "Zeche Fürst Hardenberg" at 500°, and smaller yields at 450°. (The datum 110 cubic metres per ton given in the previous paper is due to an error in measurement.)

The light oils obtained from coal at a temperature not exceeding 50° have been re-examined; the results confirm those obtained previously by the authors. The fractions boiling below 75° have a high content of unsaturated hydrocarbons, whereas paraffins are present in amount exceeding 25%. The occurrence of acetone is confirmed. The fractions of higher boiling point contain benzene, toluene, the xylenes, and phenol. There is no essential difference between the products obtained in the technical, continuous retorts and in the experimental, intermittent furnaces of Fischer and Wibaut. A possible explanation of the discrepancies between the authors' observations and those of Fischer lies in the fact that the products obtained by the latter were subjected to a preliminary treatment with aluminium chloride.

The origin of benzene in low temperature tar is discussed at length. Tetrahydrobenzene does not appear to suffer marked hydrogenation at temperatures below 500°.

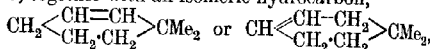
H. W.

**3:3-Dimethyl-0:1:3-bicyclohexane in Connexion with Isomeric Change in Cyclic Compounds, and the Stereoisomeric 3:5-Dibromo-1:1-dimethylcyclohexanes.** A. I. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 257—263).—Two

3:5-dibromo-1:1-dimethylcyclohexanes, one, m. p. 36.5—37.5°, and the other, b. p. 124°/10 mm.,  $n_D^{20}$  1.5301,  $d_4^{20}$  1.5771, and probably the *trans*- and *cis*-isomerides, respectively, are prepared by the action of phosphorus tribromide on 1:1-dimethylcyclohexane-3:5-diol. Both isomerides yield, on heating with zinc dust in aqueous alcohol, a mixture of 3:3-dimethyl-0:1:3-bicyclohexane,

$\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CH}_2 \end{array} \text{CMe}_2$ , b. p. 115.2—115.4°/760 mm.,  $n_D^{20}$  1.4365,

$d_4^{20}$  0.8125, together with an isomeric hydrocarbon,



which is eliminated from the mixture by oxidation with potassium permanganate.

R. T.

**The Synthesis of the Stereoisomeric 1:4-Dibromocyclohexanes.** A. E. USPENSKI and I. TURIN (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 263—274).—The synthesis of 1:4-dibromocyclohexane (Baeyer, A., 1894, i, 174) is repeated. The starting-point is diethyl succinate, which is converted successively into diethyl succinylsuccinate, 1:4-diketocyclohexane, 1:4-dihydroxycyclohexane, and 1:4-dibromocyclohexane. The dihydroxycyclohexane is obtained as a mixture of the *cis*- and *trans*-isomerides, which are separated by fractional crystallisation of their diacetyl derivatives, m. p. 34—36°, and 102—103°, respectively. These give on hydrolysis *cis*- and *trans*-1:4-dihydroxycyclohexanes, m. p. 100—102°, and 199°, respectively. Each of these, on heating in a sealed tube with hydrogen bromide, yields a mixture in the same proportions of the *cis*- and *trans*-dibromides, b. p. 137—138°/25 mm.,  $d_4^{20}$  1.7737,  $n_D^{20}$  1.5500, and m. p. 113°, respectively.

R. T.

**Catalytic Reduction of Nitro-compounds. I.  $\beta$ -Unsaturated Nitro-compounds.** E. P. KOHLER and N. L. DRAKE (*J. Amer. Chem. Soc.*, 1923, **45**, 1281—1289).—The reduction of nitrostyrene by means of hydrogen in methyl-alcoholic or ethereal solution in the presence of platinum black, or in alcohol in the presence of nickel, leads mainly to the dimeric compound,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{NO}_2$  (Sonn and Schellenberg, A., 1918, i, 9), together with *syn*- and *anti*-phenylacetaldoximes. The formation of complex compounds is largely inhibited by the presence of mineral acids. The reduction of nitrostilbene by means of hydrogen and platinum black, in ethereal solution, gives deoxybenzoin oxime.  $\beta$ -Nitro- $\alpha\alpha$ -diphenylethylene is reduced by the same method to diphenylacetalimine,  $\text{CHPh}_2 \cdot \text{CH} \cdot \text{NH}$ , long, white needles, which passes, on heating, with loss of ammonia, into a compound, probably  $\text{CHPh}_2 \cdot \text{CH}(\text{N} \cdot \text{CH} \cdot \text{CHPh}_2)_2$ , slender, white needles, m. p. 129° (decomp.). The aldimine gives benzophenone

oxidation by means of chromic acid in glacial acetic acid solution; reacts with hydroxylamine, giving diphenylacetaldoxime, and a small quantity of a substance, m. p. about 85°, and with semicarbazide acetate giving diphenylacetaldehydesemicarbazone. Dinitro- $\alpha$ -diphenylethylene is reduced in alcoholic or ethereal solution in the presence of colloidal platinum to diphenylacetone and tetraphenylacetone, together with an oil which is benzophenone on being distilled in steam. The reduction of 6-nitro-2-benzoyl-1-phenylcyclopropane in methyl-alcoholic solution by means of platinum black and hydrogen leads to the formation of  $\gamma$ -nitro- $\beta$ -phenylbutyrophenone. W. S. N.

**Halochromism. II. Halochromic Phenomena of Ethylenic Hydrocarbons and their Significance for the Theory of Halochromic Compounds.** SIEGFRIED SKRAUP and LEO FREUNDLICH *Annalen*, 1923, 431, 243—270; cf. A., 1922, i, 539).—The figure previously given for the basicity of benzhydrol is meaningless, because the latter cannot be recovered unchanged, subsequently the basicity determination; the addition of alcohol to the solution in acetic acid and sulphuric acid gives benzhydrol ethyl ether, whilst benzhydrol acetate is produced when water is added. Dilution of a halochromic solution of a mixed aliphatic-aromatic carbinol causes elimination of water, with formation of an ethylenic hydrocarbon, which gives the same coloration in acetic acid-sulphuric acid solution as the original carbinol. Moreover, the same figure for the basicity is obtained, whether the hydrocarbon or the alcohol is used, e.g. ethyldiphenylcarbinol, 0.343,  $\alpha$ -diphenylpropylene, 0.343; diphenylpropylcarbinol, 0.368,  $\alpha$ -diphenylstyrene, 0.370. It follows that either quantitative conversion into the carbinol occurs under the conditions used in the basicity determination, or the same equilibrium is attained, starting from either side,  $\text{OH}\cdot\text{CR}_2\cdot\text{CH}_2\text{R} \rightleftharpoons \text{R}_2\text{C}:\text{CHR} + \text{H}_2\text{O}$ . By addition of bromine in acetic acid solution to a solution of diphenylpropylene or the corresponding carbinol in acetic acid, or acetic acid and sulphuric acid, followed by addition of potassium iodide, and titration by means of sodium thiosulphate, it is shown that at least 86% of the solute, in the halochromic solution, exists as the unsaturated hydrocarbon. The figures so obtained are, however, too uncertain to use in calculating the basicity of pure carbinols from previous "basicity" measurements. Moreover, the unsaturated hydrocarbons themselves exhibit halochromy (see below); the results of Hess and Weltzien (A., 1922, i, 35), and particularly of Ziegler and Ochs using unsaturated carbinols (A., 1922, i, 1047), are therefore to be accepted with caution. Nevertheless, the figures quoted in the earlier paper (*loc. cit.*) may have a qualitative significance, since possibly the addition of acid to the hydrocarbon and salt formation from the carbinol may lead to the same product. The formation of the carbinol, the possibility of which is never entirely excluded when sulphuric acid is used, may be avoided, since derivatives of ethylene give colour reactions in benzene solution with stannic chloride or stannic bromide. These are true

halochromic solutions, since on dilution the intensity of the colour decreases more rapidly than the concentration. For the lemon-yellow complex from diphenylbutylene and stannic bromide the dissociation constant corresponds with the composition: 2 mol. hydrocarbon + 1 mol. halide, and has the value  $K=0.090$ . The other additive compounds examined are formed from equimolecular proportions of the components. The values of  $K$  are as follows: With stannic chloride: stilbene, yellow, 23.8; phenylstilbene, orange-yellow, 6.74;  $\alpha\alpha$ -diphenylpropylene, yellow, 2.75;  $\alpha\alpha$ -diphenylbutylene, yellowish-green, 0.280;  $\alpha\alpha$ -diphenylethylene, greenish-yellow, 0.192;  $\alpha$ -phenyl- $\alpha$ -*p*-anisylpropylene, orange, 0.0259. With stannic bromide: phenylstilbene, faintly orange, 23.8;  $\alpha\alpha$ -diphenylpropylene, orange-yellow, 12.8;  $\alpha\alpha$ -dianisylpropylene, red, 0.553;  $\alpha$ -phenyl- $\alpha$ -anisylpropylene, reddish-orange, 0.114; phenyl-*p*-anisylethylene, greenish-yellow, 1.61. Since these values for  $K$  are so high, it is not surprising that none of these additive compounds can be isolated. It is noticeable that the bromine compounds have greater dissociation constants than the chlorine derivatives (cf. Pfeiffer, A., 1914, i, 923); there is, moreover, no parallelism between ease of dissociation and colour (cf. Kaufmann, A., 1917, i, 391; Lifschitz, A., 1917, i, 558).

Pfeiffer (A., 1918, i, 62) believes that the tendency to form additive complexes shown by ketones, quinones, nitro-compounds, and acid anhydrides is a function of the whole molecule, but that addition occurs on the oxygen of the carbonyl group or of the nitro-group. The free valency of the carbon atom of the carbonyl group, or of the nitrogen atom of the nitro-group, is thus increased, this being the cause of the production of colour. Pfeiffer separates halochromic additive compounds into two classes, which are directly opposed, in respect to the effect, on colour, of substituents in the components: (1) quinhydrones, and products derived from nitro-compounds or acid anhydrides, (2) products derived from quinones, unsaturated nitro-compounds, or unsaturated ketones and acids or metallic halides. Pfeiffer can only conclude that the carbonyl group may behave in two entirely different ways, without suggesting any cause. The authors, in view of the new type of halochromism described above, regard the halochromy of quinones, unsaturated ketones, or unsaturated nitro-compounds with acids or metallic halides as a reaction of the ethylene linking, whilst the formation of quinhydrones is a reaction of the carbonyl group. In agreement with this view, the influence of substituents on colour is the same for the new additive compounds described as for the compounds of the first class.

Additive compounds exhibiting halochromy are tabulated and classified, several new examples, in addition to those already mentioned, being given. Maleic anhydride gives the following colorations: with stannic chloride, faint red; with stannic bromide, deep red; with dibenzylideneacetone, orange; with di-*p*-methoxystyryl ketone, red; with diphenylpropylene, yellow; with anisylpropylpropylene, reddish-orange; with dianisylpropylene, a deeper reddish-orange. Distyryl ketone and tetranitromethane

a lemon-yellow coloration. Di-*p*-methoxystyryl ketone and nitromethane, orange-red. Chloranil, dissolved in diphenylpropylene, phenylanisylpropylene, or dianisylpropylene, gives, respectively, a red, reddish-violet, or violet solution. In the same three solvents, *p*-benzoquinone is coloured yellow, reddish-orange, red, whilst thymoquinone is coloured yellow, yellowish-orange, reddish-orange. A fused mixture of di-*p*-methoxystyryl ketone and diphenylpropylene is scarcely coloured more deeply than the ketone itself, but an appreciable deepening of colour is observed on fusion with phenylanisylpropylene, dianisylpropylene, or di-*n*-butylpropylene. The following solutions are coloured. Distyryl ketone in benzene, lemon-yellow; in dimethylaniline, orange-yellow. Di-*p*-methoxystyryl ketone in benzene, faintly yellow; in anisole, pale yellow; in dimethylaniline, orange-yellow.

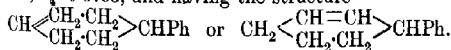
*p*-Anisyl-*dimethylcarbinol* is a colourless liquid which loses water when distilled under reduced pressure, giving  $\beta$ -*p*-anisylpropylene,  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{Me})_2\cdot\text{CH}_2$ . Phenyl-*p*-anisylpropylene, m. p.  $52^\circ$ , is obtained by the action of excess of magnesium ethyl bromide on *p*-methoxybenzophenone. The action of magnesium ethyl bromide on dimethoxybenzophenone gives di- $\alpha$ -*p*-anisylpropylene, colourless liquids, m. p.  $101^\circ$ , which not only gives the expected (red) coloration with sulphuric acid, but is oxidised by means of chromic acid to di-*p*-methoxybenzophenone. The compound described by Gattermann (A., 1889, 862) as di- $\alpha$ -*p*-anisylpropylene gives neither of these reactions; moreover, a mixed melting-point determination with the substance now described showed a depression of  $20^\circ$ . It is concluded that the material prepared by Gattermann has some other constitution.

W. S. N.

**3-Phenyl-0 : 1 : 3-bicyclohexane and the Unsaturated Cyclic Hydrocarbon,  $\text{C}_{12}\text{H}_{14}$ , in Connexion with Isomeric Change in Cyclic Compounds.** ALEXEI EUGENIEVITSCH USPENSKI (J. Russ. Phys. Chem. Soc., 1920, 51, 245—257).—3 : 5-Dibromophenylcyclohexane, b. p.  $173\text{--}175^\circ/5\text{ mm.}$ ,  $n_D^{20}$  1.5998,  $d_4^{20}$  1.5977,

prepared from 1-phenylcyclohexane-3 : 5-diol by the action of phosphorus tribromide. The dibromo-derivative, on boiling with zinc dust in aqueous alcoholic solution, yields 5-phenyl-0 : 1 : 3-bicyclohexane,  $\text{CH}_2\begin{smallmatrix} \text{CH}\cdot\text{CH}_2 \\ \text{CH}\cdot\text{CH}_2 \end{smallmatrix}\text{CHPh}$ , b. p.  $241\cdot5\text{--}242\cdot5^\circ/745\text{ mm.}$ ,

$n_D^{25}$  1.5452,  $d_4^{25}$  0.9830, contaminated with an unsaturated isomeride, which can be removed by mild oxidation with potassium permanganate. The chief product of the oxidation of the phenylcyclohexene is benzoic acid, traces of other unidentified substances being also obtained. A small quantity of a more volatile dibromide, b. p.  $155^\circ/15\text{ mm.}$ , was obtained as a by-product in the preparation of the above dibromide, and this, on treatment with zinc dust, yields a hydrocarbon,  $\text{C}_{12}\text{H}_{14}$ , b. p.  $243\cdot2\text{--}244\cdot2^\circ/756\text{ mm.}$ ,  $n_D^{25}$  1.5528,  $d_4^{25}$  0.9793, and having the structure



R. T.

**The Styphnates of some Hydrocarbons.** N. N. EPRMAN (J. Russ. Phys. Chem. Soc., 1919, 51, 353—398).—Styphnic acid (*s*-trinitroresorcinol) forms equimolecular compounds with a number of aromatic compounds; these styphnates are analogous to the picrates, but are less readily formed and less stable. The formation of these substances was studied by plotting cooling curves of mixtures of the components, and it was found that the following gave definite compounds with styphnic acid, the melting point of the dystectic being indicated in brackets: naphthalene (165.5°) (cf. Noelting and v. Salis, A., 1883, 59), phenanthrene (132.7°), acenaphthene (156.0°), retene (135.7°), and  $\alpha$ -benzyl naphthalene (doubtful, curve nearly horizontal at 134.3°). The compounds formed with the following decompose on melting and the cooling curves show a transition point indicated in brackets:  $\alpha$ -bromonaphthalene (101.2°),  $\beta$ -bromonaphthalene (131.7°),  $\alpha$ -chloronaphthalene (109.8°), fluorene (127.5°), stilbene (142.4°, very unstable). No compounds are obtained from diphenyl and dibenzyl or nitro-compounds ( $\alpha$ -nitronaphthalene, nitroacenaphthene, 1:3:5 trinitrobenzene, 2:4:6-trinitrotoluene, 2:4:6-trinitro-*m*-xylene) whilst diphenylmethane and triphenylmethane are only partly miscible with styphnic acid in the molten state. G. A. R. K.

**The Stepwise Addition of Hydrogen to Tetraphenylallene.** D. VORLÄNDER and PAUL WEINSTEIN (Ber., 1923, 56, [B], 1122—1124).—Although the constitution of tetraphenylallene,  $\text{CPh}_2\text{=C=CPh}_2$ , has been placed beyond doubt by its synthesis and degradation (cf. Vorländer and Siebert, A., 1906, i, 345; Vorländer, Osterburg and Meyer, this vol., i, 682), the presence of the two unsaturated linkings has not previously been directly established by additive reactions. It is now shown that the hydrocarbon may be reduced by regulated treatment with a mixture of glacial acetic acid, hydriodic acid (*d* 1.7), and red phosphorus to tetraphenylpropylene,  $\text{CHPh}_2\text{=CH}\cdot\text{CPh}_2$ , m. p. 127—128° (cf. Vorländer and Siebert, *loc. cit.*) which may be reduced further to tetraphenylpropane. The unsaturated compound can be supercooled to an unusual degree. It is oxidised by chromic acid in the presence of glacial acetic acid to benzophenone and diphenylacetic acid.

Tetraphenylallene, dissolved in carbon tetrachloride, is converted by short treatment with chlorine into the chloride,  $\text{C}_6\text{H}_4\text{<CPh}_2\text{>CCl}$ , m. p. 167°.

Tetraphenylallene and nitrogen trioxide dissolved in cold benzene yield a colourless, crystalline compound,  $\text{C}_{24}\text{H}_{20}\text{O}_3\text{N}_2$ , m. p. 141—142°, which is possibly a nitrosite, from which, however, tetraphenylallene cannot be recovered. It is converted by alcoholic stannous chloride solution or by hydrogen chloride in the presence of alcohol or glacial acetic acid into the dioxide,  $\text{Ph}_2\text{C}>\text{O}<\text{CPh}_2$ ,

m. p. 198°, which is identical with the product obtained by Vorländer and Siebert (*loc. cit.*) by the action of chromic acid on tetraphenylallene. H. W.

The Stereochemistry of the Hexahydrotoluidines [Methylcyclohexylamines]. A. SKITA (*Ber.*, 1923, 56, [B], 1014—1023). It has been shown previously (Skita and Berendt, A., 1920, 27) that the catalytic hydrogenation of the toluidines in the presence of platinum leads in each case to the production of two methylcyclohexylamines which are separable in the form of their crystalline benzoyl derivatives. The latter compounds have now been hydrolysed to the corresponding free bases which, however, are not readily prepared in this manner, as it involves the expenditure of much time and material. It is more convenient to use the acetotoluidines as the starting points, since these substances are converted into the corresponding *cis*-hexahydro-derivatives when hydrogenated in the presence of colloidal platinum, chloroacetic acid, and a sufficiency of hydrochloric acid, and into the *trans*-hexahydro-compounds when treated with hydrogen and colloidal platinum in neutral, aqueous solution. The methylcyclohexylamines are colourless liquids which readily absorb carbon dioxide from the atmosphere, the ability being more pronounced in the *trans*- than with the *cis*-amines. The isomerides differ from one another in odour, that of the *cis*-series being penetratingly ammoniacal, whereas that of the *trans*-compounds resembles conine. The electrical conductivity is the same for each isomeride. When treated with nitrous acid the *cis*- and *trans*-amines pass into the corresponding *cis*- and *trans*-methylcyclohexanols (cf. this vol., 460). [With HANS HÄUBER and WILHELM SCHARENBERG.]—The following individual substances are described: *cis*-Aceto-*o*-methylcyclohexylamide, b. p. 162—163°/18 mm., m. p. 82°, the corresponding meta-derivative, granular crystals, b. p. 156·5—157·5°/15 mm., m. p. 74—75°, and the para-compound, pointed needles, b. p. 160·5°/18 mm., m. p. 79°, *trans*-aceto-*o*-methylcyclohexylamide, b. p. 153—155°/17 mm., m. p. 57°, the corresponding meta-derivative, b. p. 159°/20 mm., m. p. 63°, and para-compound, b. p. 156—158°/17 mm., m. p. 68—69°. The acetyl derivatives are hydrolysed by concentrated hydrochloric acid at 130—140°, to the free amines of which the complete series is described as follows: *cis*-methylcyclohexylamine, b. p. 153·5—154·5° (corr.),  $d_4^{20}$  0·8778,  $n_D^{20}$  1·4688 (benzoyl derivative, m. p. 107°; phenylcarbamide compound,  $C_{14}H_{20}ON_2$ , m. p. 85°); *trans*-*o*-methylcyclohexylamine, b. p. 149·7—150·2° (corr.),  $d_4^{20}$  0·8688,  $n_D^{20}$  1·4650 (benzoyl derivative, m. p. 146°; phenylcarbamide compound, m. p. 130—131°); *cis*-*m*-methylcyclohexylamine, b. p. 152·7—153·4°,  $d_4^{20}$  0·8552,  $n_D^{20}$  1·4538 (benzoyl derivative, m. p. 98°; phenylcarbamide compound, m. p. 138·5°); *trans*-*m*-methylcyclohexylamine, b. p. 151·5—152·5° (corr.),  $d_4^{20}$  0·8572,  $n_D^{20}$  1·4547 (benzoyl derivative, m. p. 127°; phenylcarbamide compound, m. p. 178—179°); *cis*-*p*-methylcyclohexylamine, b. p. 153·3—153·7° (corr.),  $d_4^{20}$  0·8567,  $n_D^{20}$  1·4559 (benzoyl derivative, m. p. 116°; phenylcarbamide compound, m. p. 102°); *trans*-*p*-methylcyclohexylamine, b. p. 151·5—151·9° (corr.),  $d_4^{20}$  0·8543,  $n_D^{20}$  1·4550 (benzoyl derivative, m. p. 180°; phenylcarbamide compound, m. p. 176°).

The methylcyclohexylamines have also been prepared by the

reduction of the corresponding methylcyclohexanoneoximes, the *cis*-compounds being formed when the action is effected by sodium amalgam in the presence of alcohol and glacial acetic acid, and the *trans*-derivatives resulting when sodium amalgam and alcohol are used. The physical constants of the substances themselves and their derivatives agree with those of the compounds prepared as described in the preceding paragraph. The following derivatives are also described: *cis*-*o*-methylcyclohexylthiocarbimide, a pungent smelling liquid, b. p. 228–229°/769 mm.,  $d_4^{20}$  0.9680,  $n_D^{20}$  1.5336, and *phenyl*-*cis*-*o*-methylcyclohexylthiocarbimide,  $C_{14}H_{20}N_2S$ , colourless leaflets, m. p. 114°; *trans*-*o*-methylcyclohexylthiocarbimide, b. p. 224–225°/770 mm.,  $d_4^{20}$  0.9620,  $n_D^{20}$  1.5303, and the corresponding 3-*phenyl*thiocarbimide, leaflets, m. p. 145°; *cis*-*m*-methylcyclohexylthiocarbimide, b. p. 226–227°,  $d_4^{20}$  0.9479,  $n_D^{20}$  1.5204, and the corresponding *phenyl*thiocarbimide, m. p. 105–106°; *trans*-*m*-methylcyclohexylthiocarbimide, b. p. 224.5–225.5°,  $d_4^{20}$  0.9487,  $n_D^{20}$  1.5206, and the corresponding *phenyl*thiocarbimide, m. p. 94–95°, after softening at 90°; *cis*-*p*-methylcyclohexylthiocarbimide, b. p. 227–228°/765 mm.,  $d_4^{20}$  0.9470,  $n_D^{20}$  1.5208, and the corresponding *phenyl*thiocarbimide, m. p. 149°; *trans*-*p*-methylcyclohexylthiocarbimide, b. p. 225.5–226.5°/765 mm.,  $d_4^{20}$  0.9450,  $n_D^{20}$  1.5200, and the corresponding *phenyl*thiocarbimide, m. p. 159°.

*cis*-*p*-Methylcyclohexylmethylamine, prepared by the action of an ethereal solution of methyl sulphate on *cis*-*p*-methylcyclohexylamine, has b. p. 157.5–158.5°/766 mm.,  $d_4^{20}$  0.8485,  $n_D^{20}$  1.4529; its *picrate* has m. p. 179°. It is transformed by an ethereal solution of methyl iodide into *cis*-*p*-methylcyclohexyldimethylamine, b. p. 160–161°/767 mm.,  $d_4^{20}$  0.8355,  $n_D^{20}$  1.4507 (*picrate*, yellow crystals, m. p. 181°). *trans*-*p*-Methylcyclohexylmethylamine has b. p. 154–155°/767 mm.,  $d_4^{20}$  0.8440,  $n_D^{20}$  1.4522; it yields a *picrate*, m. p. 182.5°. *trans*-*p*-Methylcyclohexyldimethylamine has b. p. 156.5–157°/764 mm.,  $d_4^{20}$  0.8320,  $n_D^{20}$  1.4494 (*picrate*, m. p. 184°). H. W.

**Solubility of Tetranitroaniline in Organic Solvents.** C. A. TAYLOR and W. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1923, 45, 1218–1220).—The solubility of tetranitroaniline has been determined in water, methyl alcohol, ethyl alcohol, diethyl ether, acetone, chloroform, carbon tetrachloride, carbon disulphide, and toluene at 0° and in benzene at 3.9°. The following solubilities in grams per 100 g. of solvent are recorded: water, 0.007; methyl alcohol, 0.45; ethyl alcohol, 0.34; diethyl ether, 0.081; acetone, 7.50; chloroform, 0.010; carbon tetrachloride, 0.0036; carbon disulphide, 0.0056; benzene (3.9°) 0.13; and toluene, 0.188. Attempts to determine the solubility at higher temperatures were unsuccessful, owing to the tendency of tetranitroaniline to decompose. The solubility is slightly lower than that of tetryl in the same solvents (this vol., i, 315, 320). J. F. S.

**The Electrical Conductivity, Viscosity and Diagrams of State of the Systems formed by Benzoic Acid with Diphenylamine, the Naphthylamines and Quinoline.** III. ALEXANDER BASILEVITSCH BASKOV (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 589–618; cf. A., 1913, ii, 1016; 1915, ii, 408).—The investigation of

the above systems by the thermal method shows that benzoic acid does not form compounds with diphenylamine, or  $\alpha$ - or  $\beta$ -naphthylamines, simple eutectics being obtained corresponding with about 8, 25, and 50 mol. % of benzoic acid, respectively. The system benzoic acid-quinoline shows a definite transition point corresponding with 23° and 50 mol. % of the components, whilst the eutectic point corresponds with -40° and 17 mol. % of benzoic acid.

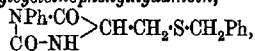
The conductivity curves of the systems consisting of benzoic acid with the naphthylamines show breaks corresponding with 50 mol. % of acid, but these are due to the formation of naphthalides, which were isolated; the conductivity of the system benzoic acid-diphenylamine could not be measured at all.

The conductivity, viscosity, and density measurements on the system benzoic acid-quinoline point to the existence of a compound, but its composition corresponds with 66.6% of acid, not 50%; the same is true of the system benzoic acid-pyridine (cf. A., 1915, ii, 408). It is suggested that compounds of the type of acid salts may be formed at higher temperatures and serve as electrolytes; or the excess of benzoic acid may serve as a dielectric medium, although in that case it is difficult to understand why the point of maximum conductivity should correspond so exactly with a definite molecule complex.

G. A. R. K.

**Some Derivatives of Cystine and Cysteine.** GEORGE J. SIPLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1923, 55, 671—686).

—The following derivatives have been prepared: *diphenylacetylcystine*, short rods or needles, m. p. 119—121°; *phenylacetylbenzylcystine*,  $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , bunches of long, fine needles, m. p. 87—89°; *phenylcarbamylbenzylcystine*,  $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{H}$ , feathery crystals, m. p. 145—146.5°; *benzylcystinephenylhydantoin*,



fine needles, m. p. 118—119.5°, *acetylbenzylcystine*, fine needles, m. p. 156—157°; *p-chlorobenzylcystine*, m. p. 219—220°; *phenylcarbamylcystine*, fine, short needles, m. p. 134—136°. E. S.

**Picryl Sulphide. Study of the Binary System Trinitroanisole-Picryl Sulphide.** CHAUMÉIL and V. THOMAS (*Compt. rend.*, 1923, 176, 1323—1325).—Thermal study of the binary mixture gave a normal curve which is shown diagrammatically. Certain abnormal results were also obtained in the case of mixtures containing more than 90% of trinitroanisole. On solidification, the rise of the thermometer occurred in two separate stages, but no intermediate maximum was detected. The authors put forward the hypothesis of formation of an unstable system which separates into trinitroanisole and the eutectic mixture at a temperature below that corresponding with the eutectic temperature of the stable system.

H. J. E.

**Electrolytic Preparation of o-Aminophenol. Effect of Cathode Materials.** O. W. BROWN and J. C. WARNER (*J. Physical Chem.*, 1923, 27, 455—465).—The electrolytic reduction

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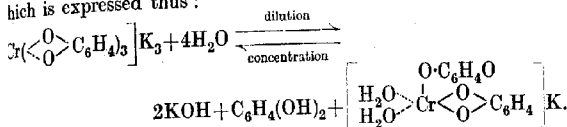
of *o*-nitrophenol in 15% sodium hydroxide solution has been investigated, using cathodes of various materials under a series of different conditions. It is shown that at low current densities (1—2 amps. per dm.<sup>2</sup>) copper, zinc, zinc amalgam, and nickel are the most efficient cathodes for this reduction. At current densities from 4.0—10.0 amps. per dm.<sup>2</sup> lead cathodes give the highest yield (95.4%), whilst zinc and zinc amalgam give a little lower yield (about 93%). Except in the case of lead, increase in the current density causes a decrease in the yield, but in no case is the decrease greater than 15% for an increase from 1 amp. to 10 amps. Discharge potentials and depolarisation values are not criterions of the usefulness of a material as cathode in carrying out this reduction. The efficiency of a metal in the reduction of *o*-nitrophenol to *o*-aminophenol is generally reduced slightly by amalgamation. Since the factors on which the efficiency of a material as an electrode depends are many and variable, the best method of ascertaining what is the most suitable material for an electrode in any given reduction appears to be that of an experimental test under various conditions of temperature, current density, and concentration. J. F. S.

**Acyl Derivatives of *o*-Aminophenol.** R. E. NELSON and H. L. DAVIS (*Proc. Indiana Acad. Sci.*, 1921, 201—202; cf. Ransom, A., 1900, i, 218; Stieglitz and Upson, A., 1904, i, 575; Ransom and Nelson, A., 1914, i, 269; Raiford, A., 1920, i, 156).—When the groups COR- and CO-OR- are introduced into *o*-aminophenol, the latter group always becomes attached to the nitrogen atom, regardless of the order of introduction. If the group COR- is at first in that position, it is removed to the oxygen atom when the group CO-OR- is introduced. CHEMICAL ABSTRACTS.

**Preparation of 2-Hydroxy-1-arylnaphthylamines.** SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE ST. DENIS, ANDRÉ RASUL WAHL, and ROBERT LANTZ (Brit. Pat. 182084).—2-Hydroxy-1-arylnaphthylamines are obtained by heating primary aromatic amines with  $\alpha$ -chloro- or  $\alpha$ -bromo- $\beta$ -naphthols, either in presence or absence of a suitable solvent and with or without the addition of powdered zinc, tin, iron, lead, or copper, which accelerates the reaction but at the same time favours the formation of secondary products. Example: 1 part of  $\alpha$ -chloro- $\beta$ -naphthol is boiled for three to four hours with 5 parts of aniline, the excess of aniline is removed by steam distillation, the residue washed with dilute sodium hydroxide, the alkaline solution acidified, and the precipitated 2-hydroxy-1-phenylnaphthylamine, m. p. 153—154°, thus obtained purified by recrystallisation first from benzene, and then from a mixture of acetic and formic acids. 2-Hydroxy-1-p-tolynaphthylamine, similarly prepared, has m. p. 137—138°. G. F. M.

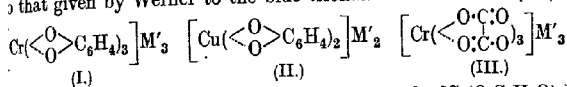
**Compounds of Tervalent Chromium and of Bivalent Copper with Pyrocatechol.** R. WEINLAND and EDMUND WALTZER (*Z. anorg. Chem.*, 1923, 126, 141—166; cf. A., 1912, i, 184, 445, 850).—When excess of ammonia is added to a solution of pyrocatechol and green chromium chloride hexahydrate, the precipitate

chromium hydroxide which first forms is dissolved to a dark green solution, owing to the formation of a complex ion containing catechol. Many salts of this type have been isolated. They are green, crystalline solids, with the exception of those containing pyridine, which are green with a tinge of yellow, and those containing a chloropentamminechromic complex, which exhibit reddish-green dichroism; they become dark coloured on exposure to the air. The alkali, barium, and guanidine salts are easily soluble in water, the barium-ammonium salt is less soluble, and the remainder are sparingly soluble. Dilution of the aqueous solution causes the green colour to change to Bordeaux red—a reversible reaction which is expressed thus:

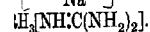
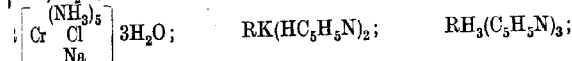


Similar copper salts can be obtained which are olive-green in colour, except the basic sodium salt, which is yellowish-green.

The constitution assigned to these compounds (I, II) is similar to that given by Werner to the blue trioxalatochromic salts (III).



The following salts are described: Chromium salts  $[\text{Cr}(\text{O} \cdot \text{C}_6\text{H}_4)_3]$   $\text{R}$ ;  $\text{R}(\text{NH}_4)_3 \cdot \text{H}_2\text{O}$ ;  $\text{R}(\text{NH}_4)_2 \cdot \text{H}$ ;  $\text{R}(\text{NH}_4)_2 \cdot \text{H}_2\text{O}$ ;  $\text{R}\text{K}_3 \cdot \text{H}_2\text{O}$ ;  $\text{R}\text{H}_2\text{K}$ ;  $\text{R}\text{Na}_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{R}\text{Li}_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{R}\text{Mg} \cdot \text{NH}_4$ ;  $\text{R}\text{KCa} \cdot 2\text{H}_2\text{O}$ ;  $\text{R}\text{Sr}_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{R}_2\text{Ba}_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{R}(\text{NH}_4)\text{Ba} \cdot 6\text{H}_2\text{O}$ ;  $\text{RNaBa} \cdot 6\text{H}_2\text{O}$ ;  $\text{RKBa} \cdot 6\text{H}_2\text{O}$ ;  $\text{RMnK}$ ;  $\text{RCoK} \cdot 6\text{H}_2\text{O}$ ;  $\text{R}[\text{Al}(\text{H}_2\text{O})_6]_3$ ;  $\text{R}[\text{Cr}(\text{H}_2\text{O})_6]_3$ ;



Copper salts  $[\text{Cu}(\text{O} \cdot \text{C}_6\text{H}_4)_2] = \text{R}'$ ;  $\text{R}'(\text{NH}_4)_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{R}'(\text{NH}_4)_2$ ;  $\text{R}'\text{Li}_2 \cdot 9\text{H}_2\text{O}$ ;  $\text{R}'\text{K}_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{R}'\text{Na}_2 \cdot \text{NaOH} \cdot 7\text{H}_2\text{O}$ ;  $\text{R}'\text{Ba}$ ;  $\text{R}'\text{Mn} \cdot 4\text{H}_2\text{O}$ ;  $\text{R}'\text{Co} \cdot 4\text{H}_2\text{O}$ ;  $\text{R}'\text{H}_2(\text{NH}_3\text{C}(\text{NH}_2)_2)_2$ ;  $\text{Cu}(\text{O} \cdot \text{C}_6\text{H}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$ . H. H.

**An Explosive (Lead Trinitroresorcinoxide).** E. HERZ (U.S. Pat. 1443328).—Lead trinitroresorcinoxide,  $\text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{O}_2\text{Pb}$ , is prepared by adding a boiling solution of 650 g. of lead nitrate in 4 litres of water to a boiling solution of 245 g. of resorcinol and 80 g. of crystalline sodium carbonate in 12.8 litres of water and 7 c.c. of glacial acetic acid. It is a dark orange-coloured, granular, crystalline powder,  $d$  3.09, and is a powerful explosive (cf. Brit. Pat. 87012/1921).

CHEMICAL ABSTRACTS.

**A Verification of the Antioxygenising Power of Polyphenols: The Relation between "Fastness to Light" of Dyes on Fibres and the Presence in their Molecule of the Ortho or Para Diphenolic Function.** ALFRED GILLET (*Compt. rend.*, 1923, 176, 1402—1405).—A study of the stability of dyes

towards atmospheric oxidation from the point of view of chemical constitution shows that it is apparently correlated with the existence in the molecule of an ortho- or para-dihydroxyphenol. This function is possibly analogous to the anti-oxygenising properties of the dihydroxyphenols described by Moreu and Dufrasse (this vol., i, 91), but in the dyes the replacement of hydroxyl by other groups such as  $-N=NAr$ ,  $-NHAr$ ,  $-NHAc$ ,  $-OAr$ ,  $-SH$ ,  $-SAr$  also results in stable substances. The author points out that, in addition to the view of such groups as auxochromes, they should also be considered in respect of their stabilising properties.

H. J. E.

**Molecular Rearrangements accompanying the Dehydration of Phenylethyl- $\beta$ -disubstituted Primary Alcohols.** (Mau)

PAULINE RAMART and J. BLONDEAU (*Compt. rend.*, 1923, 176, 1320—1323; cf. Haller and Bauer, A., 1918, i, 428; Haller and Ramart, *Compt. rend.*, 1922, 174, 1211).—Further study of the dehydration of disubstituted primary alcohols of the type  $CR^1R^2Ph\cdot CH_2\cdot OH$  shows that in each case the principal substance produced is  $CR^1R^2CHPh$ . In addition to the migration of the phenyl group, a small proportion of the resulting product is formed by similar shifting of another substituting group to yield either  $CR^1Ph\cdot CHR^2$  or  $CR^2Ph\cdot CHR^1$ . The alcohols investigated were  $\beta$ -phenyl- $\beta$ -methyl- $\alpha$ -butanol,  $\beta$ -phenyl- $\beta$ -ethyl- $\alpha$ -butanol, and  $\beta$ -benzoyl- $\beta$ -phenyl- $\alpha$ -butanol.

H. J. E.

**A New Series of Hypnotics: the Aryldialkylglycols**

M. TIFFENEAU and H. DORLENCOURT (*Compt. rend.*, 1923, 176, 1343—1346; cf. A., 1907, i, 130).—The aryldialkylglycols exhibit hypnotic properties as shown by experiments on dogs, mice, and sticklebacks. These properties appear to be due to the glycol group, they are increased by the presence of the three substituents and appear to vary with the number of carbon atoms in the molecule. The relative positions of the substituents also affect the results obtained.

H. J. E.

**Retrograde Precipitation of Salts of Aromatic Acids**

A. SMITS (*Z. physikal. Chem.*, 1923, 104, 481—486).—The author shows that the results obtained by Ephraïm (this vol., i, 32), on the precipitation of salts of aromatic acids are readily explained on the basis of the theory of allotropy.

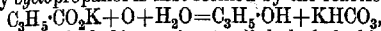
J. F. S.

***n*-Butyl *p*-Aminobenzoates.** R. ADAMS and E. H. VOLWILE

(U.S. Pat. 1440652).—*n*-Butyl *p*-nitrobenzoate, white plates m. p. 35°, is prepared by reaction between *n*-butyl alcohol and *p*-nitrobenzoic acid in the presence of sulphuric acid. Reduction with iron and hydrochloric acid yields *n*-butyl *p*-aminobenzoate m. p. 57—58.5°, which is a local anæsthetic. *n*-Butyl 3:5-dinitrobenzoate is similarly reduced to *n*-butyl 3:5-diaminobenzoate, viscous liquid which does not solidify at the ordinary temperature (monohydrochloride, m. p. 255° [decomp.]).

CHEMICAL ABSTRACTS.

**The Behaviour of Alkali Salts of cycloPropanecarboxylic acid at the Anode and the Thermal Decomposition of Perbutyric Acid.** FR. FICHTER and HANS REEB (*Helv. Chim. Acta*, 1923, 6, 450—457).—When potassium cyclopropanecarboxylate is electrolysed using a platinum anode, preferably in presence of excess of cyclopropanecarboxylic acid, the allyl ester of cyclopropanecarboxylic acid is formed, together with a considerable quantity of high boiling, presumably polymerised products. Apparently cyclopropanol is first formed by the reaction



but this unstable alcohol isomerises to allyl alcohol which in presence of excess of the carboxylic acid forms the ester. For comparison with the product of electrolysis, allyl cyclopropanecarboxylate was prepared from silver cyclopropanecarboxylate and allyl chloride. It is a colourless, mobile oil of pleasant odour, b. p. 154—155°. It is accompanied by a high-boiling fraction similar to that obtained with the electrolytically prepared ester. The formation of cyclopropanol and subsequently of ester is to be attributed to the decomposition of per-acid formed at the anode. In confirmation of this, it is found that, by the thermal decomposition of perbutyric acid, isopropyl butyrate is formed, and among the decomposition products of a preparation of cyclopropaneper-carboxylic acid, allyl cyclopropanecarboxylate was recognised.

E. H. R.

**Hydroxynaphthoic Acids.** I. FRANK ALBERT ROYLE and JACK ARNOLD SCHEDLER (*T.*, 1923, 123, 1641—1647).

**Abietic Acid.** A. W. SCHORGER (*J. Amer. Chem. Soc.*, 1923, 45, 1339—1340).—Exception is taken to the view (Steele, A., 1922, 44, 739) that the crystallisation of rosin is due to hydration, and that rosin consists of abietic anhydride (Knecht and Hibbert, A., 1919, i, 38), and has not been crystallised from anhydrous solvents, for the following reasons. The solvent previously employed (A., 1915, 37, 431) was petroleum naphtha, dried over calcium chloride. From this solvent it is possible to crystallise rosin which has been (1) heated at 220—225° under 25 mm. for thirty minutes, or (2) distilled under reduced pressure in such a way that any water present could not be condensed. Moreover, rosin becomes opaque on the surface more rapidly when kept in water than when kept in sulphuric acid, whereas the hydration of an anhydride should proceed more rapidly in the presence of mineral acid. The loss of weight observed by Knecht and Hibbert when abietic acid is heated at 180° in an atmosphere of carbon dioxide has not been shown to be due entirely to loss of water.

W. S. N.

**Racemic apoFenchocamphoric Acid.** SERGEI SEMENOVITSCH SAMETKIN and (Mlle) ANNA MICHAILOVNA CHUCHRIKOVA (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 426—428; cf. *ibid.*, 1915, 47, 433).—*trans*-apoFenchocamphoric acid on treatment with acetyl chloride gives an anhydride, m. p. 136—137°, which on solution in alkali hydroxides and reprecipitation by acids regenerates the *cis*-acid; the anilide, m. p. 155—157°, and dianilide, m. p. 148—150°, were

also prepared, the former probably consisting of a mixture of the anilides of the *cis*- and *trans*-isomerides. *trans*-apo*Fenchocampyphoric* acid, m. p. 147—148°, is prepared by the action of concentrated hydrochloric and acetic acids on the *cis*-isomeride, and does not form an anhydride with acetyl chloride. The *anilide*, m. p. 133—142°, also a mixture of isomerides, and the *dianilide*, m. p. 215—216°, were prepared.

R. T.

**Derivatives of cycloHexane-3:6-dione-1:2-dicarboxylic Acid.** BURCKHARDT HELFERICH and HELLMUT GUSTAV BODENBENDER (*Ber.*, 1923, 56, [B], 1112—1116; cf. A., 1921, i, 185).—Methyl cyclohexane-3:6-dione-1:2-dicarboxylate is converted by acetic anhydride in the presence of concentrated sulphuric acid into the corresponding *diacetate*,  $C_{14}H_{16}O_8$ , m. p. 87—88°. It gives a *dithallium* salt. Methyl 2-benzylcyclohexane-3:6-dione-1:2-dicarboxylate crystallises in short, thick prisms, m. p. 106° (corr.) after softening at 105°; it yields a *diphenylhydrazone*,  $C_{23}H_{30}O_4N_4$ , m. p. (indefinite) 75—80°.

cycloHexane-3:6-dione-1:2-dinitrile,  $CO \begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}(\text{CN}) \text{---} \text{CH}(\text{CN}) \end{array} CO$ , crystallises in slender, colourless needles, m. p. 160—170° (decomp.) after darkening at about 100°. The *sodium* salt,  $C_8H_8O_4N_2Na_2$ , and the *thallium* salt,  $C_8H_8O_4N_2Tl_2$ , were analysed. The *semicarbazone*,  $C_{10}H_{12}O_2N_3$ , darkens at about 200°, but does not melt below 280°. With phenylhydrazine in acetic acid solution (80%), the dinitrile yields a *compound* (? *diphenylhydrazone*),  $C_{20}H_{18}N_6$ , a reddish-brown, amorphous precipitate, m. p. (indefinite) 226—232° after becoming discoloured at about 180°. The crystalline *diacetate*,  $C_{12}H_{16}O_4N_2$ , has m. p. 162° (corr.). cycloHexane-3:6-dione-1:2-dinitrile is converted by boiling dilute sulphuric acid into cyclohexane-1:4-dione and by diazomethane in ethereal solution into the *dimethyl ether*,  $OMe \cdot C \begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} C \cdot OMe$ , m. p. 202° (corr.) after softening at 200°. The latter substance is converted by sulphuric acid into cyclohexane-1:4-dione and by aqueous potassium hydroxide solution into a mixture of 2:5-dimethylgentisic acid and succinic acid.

H. W.

**Bile Acids. IX.** MARTIN SCHENCK (*Z. physiol. Chem.*, 1923, 128, 53—58).— $\alpha$ -Diketocholanic acid reacts with hydrazine to yield the *dioxime*,  $C_{24}H_{38}O_4N_2$ , decomp. 184—187°, forming characteristic double pyramids. When heated with sulphuric acid, this yields an isomeric *compound*, decomp. 196—197°, microscopic bundles of needles. From the dioxime, when heated with 25% hydrochloric acid, a *compound* is formed, m. p. 188—189°, insoluble in acid, whilst the isomeric compound yields no such compound insoluble in acid under similar conditions. W. O. K.

**Preparation of Intermediate Products for Dyes.** [4:4'-Dihydroxy-1:1'-ketodinaphthalene-3:3'-dicarboxylic Acid, and  $\alpha$ -Naphthol-2:4-dicarboxylic Acid.] SOCIETY OF CHEMICAL INDUSTRY IN BASLE (*Brit. Pat.* 195513, addition to 172177).—In the preparation of trihydroxytrinaphthylmethane dyes

from  $\alpha$ -naphthol- $\beta$ -carboxylic acid and a tetrahalogen derivative of methane the above two substances are also formed as by-products. Their formation at the expense of the dye is favoured by increasing the proportion of carbon tetrachloride, using potassium hydroxide for neutralising the liberated hydrogen chloride, and carrying out the reaction in a highly diluted medium. The keto-acid can readily be separated from the naphtholdicarboxylic acid by taking advantage of the difference in solubility of the alkali and alkaline-earth salts of the two acids. Thus the mother-liquor from the dye separation may be acidified, the precipitate dissolved in sodium carbonate solution, and the disodium salt of the keto-acid precipitated by the addition of sodium chloride. The keto-acid itself is a white powder, which decomposes without melting at about  $259^{\circ}$ . The mother-liquor from the keto-acid separation is then acidified, and the precipitate extracted with boiling baryta water. Acidification of the extract causes the precipitation of  $\alpha$ -naphthol-2 : 4-dicarboxylic acid, a whitish powder, decomp. about  $286^{\circ}$ .  
G. F. M.

### Substitution in Vicinal Trisubstituted Benzene Derivatives.

I. WILLIAM DAVIES (T., 1923, 123, 1575—1593).

The Isomeric Transformations of Cyclic 2-Monochloro-ketones. II. A. E. FAVORSKI and VADIM NIKOLAEVITSCH BOSHOVSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 582—588).—In the first part (A., 1915, i, 411) it was shown that 2-chlorocyclohexanone is converted by alcoholic potassium hydroxide into cyclopentanecarboxylic acid, 2-chloromethylcyclohexanone behaving in a similar manner. The reaction has now been extended to 2-chlorocyclopentanone and 2-chlorosuberone.

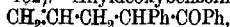
The former compound is readily obtained and boils at  $80^{\circ}$ — $81^{\circ}/17$  mm. (cf. Koetz, A., 1913, i, 1200; Godchot and Taboury, *ibid.*, 278),  $d_4^{20}$  1.2061,  $d_4^{20}$  1.1854,  $[R_L]_D$  28.08; it is significant that the action of alcoholic alkali on it leads to complete resinification, no trace of cyclobutanecarboxylic acid being obtained.

2-Chlorosuberone is obtained in 56% yield, b. p.  $106^{\circ}$ — $107^{\circ}/24$  mm. (cf. Koetz, *loc. cit.*),  $d_4^{20}$  1.1513,  $d_4^{20}$  1.1328,  $[R_L]_D$  37.18; a dichlorosuberone, m. p.  $55^{\circ}$ — $56^{\circ}$  after crystallisation from light petroleum, is obtained as a by-product. By the action of alcoholic potassium hydroxide, a 50% yield of cyclohexanecarboxylic acid is obtained from the monochloro-ketone, m. p.  $29.5^{\circ}$ — $30.5^{\circ}$ . A small amount of cyclohexan-2-olcarboxylic acid, m. p.  $108^{\circ}$ — $109^{\circ}$  (A., 1913, i, 728), is also produced in this reaction. The formation of the hydroxy-acid is due to oxidation, as is shown by carrying out the reaction with 2-chlorocyclohexanone in the presence of copper sulphate, when cyclopentan-2-olcarboxylic acid is almost the sole product of the reaction. In the reaction with 2-chlorocyclohexanone (*loc. cit.*), a small amount of a neutral oil was produced. This is now shown to be ethyl cyclopentanecarboxylate, b. p.  $172^{\circ}$ — $174^{\circ}/752$  mm., and can be made the principal product of the reaction by avoiding excess of alkali; a little 2-cyclohexanolone,

m. p. 118—119°, and cyclopentan-2-olcarboxylic acid are also produced. G. A. R. K.

**Dehydration of Secondary-Tertiary  $\alpha$ -Alcohols; Derivatives of Hydrobenzoin.** I. STEFAN NIKOLAEVITSCH DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 97—123).—Some observations previously published (this vol., i, 579) are repeated, with some additions. Triphenylethanol on reduction with hydriodic acid undergoes molecular rearrangement, yielding  $\alpha\beta$ -triphenylethane; with phosphorus pentachloride, triphenylchloroethylene is produced. R. T.

**Allyldeoxybenzoin.** S. N. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 123—132).—Allyldeoxybenzoin,



is prepared by the action of allyl iodide on deoxybenzoin in the presence of sodium ethoxide. The product thus obtained is a mixture of two isomerides; one an oil, b. p. 178—179°/9—10 mm.,  $d_4^{20}$  1.0742,  $n_D^{20}$  1.57989, and the other a solid, m. p. 35.5°, b. p. 178—179°/9—10 mm. Both give on oxidation  $\beta$ -benzoyl- $\beta$ -phenylpropionic acid; on heating with alcoholic potash, they yield a mixture of hydrocarbons, containing stilbene and the three phenylbutenes. Two semicarbazones of allyldeoxybenzoin, m. p. 177—178° and 117.5°, are obtained, and two oximes, m. p. 140—141° and 127°, respectively. R. T.

**Disubstituted Deoxybenzoins.** I. S. N. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 133—138).—Two methods for the preparation of the hitherto unknown disubstituted deoxybenzoins are described. The first of these consists in heating phenyldeoxybenzoin with solid sodium hydroxide and ethyl iodide in a sealed tube. Better results are obtained by first forming the sodium salt of phenyldeoxybenzoin and then heating this with ethyl iodide in a sealed tube. By the former method, a 15% yield and by the latter method a 40% yield of ethyldeoxybenzoin, m. p. 120°, are obtained. Attempts at the preparation of the oxime and semicarbazone of this substance were unsuccessful. Reduction with sodium ethoxide yields  $\alpha$ -hydroxy- $\alpha\beta$ -triphenylbutane. R. T.

**The Chemistry of the Three-carbon System. I. The Influence of the cycloHexane Ring on the  $\alpha\beta$ - $\gamma$ -Change.** STANLEY FRANCIS BIRCH, GEORGE ARMAND ROBERT KOX, and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS [with an Introductory Note by J. F. THORPE] (*T.*, 1923, 123, 1361—1374).

**The Action of Sodium on Diphenylacetic Ester.** D. VORLÄNDER and EDGAR RACK (*Ber.*, 1923, 56, [B], 1125—1129).—To explain the production of tetraphenylallene by the dry distillation of barium diphenylacetate, Vorländer and Siebert (*A.*, 1906, i, 345) have been led to presume the intermediate formation of the then unknown tetraphenylacetone [dibenzhydryl ketone],  $\text{CHPh}_2\cdot\text{CO}\cdot\text{CHPh}_2$ . The substance, m. p. 134°, has now been

prepared by the action of sodium on diphenylacetic ester in the molten state or in ethereal solution. It is identical with the product obtained by Staudinger (A., 1911, i, 306) by the action of alkalis on diphenylketen. It can be distilled unchanged over phosphoric oxide, calcium oxide, or barium carbonate. It crystallises unchanged from acetic anhydride, thionyl chloride, or phosphoryl chloride and does not react readily with phosphorus pentachloride. It does not unite with bromine, neither does it exhibit the characteristic ketonic reactions with semicarbazide, phenylhydrazine, or hydroxylamine. When passed through a red hot tube, it gives a mixture of products containing some tetraphenylmethane, m. p. 207°. When distilled with zinc dust, it gives diphenylmethane and other substances. It is oxidised by chromic acid in the presence of glacial acetic acid to benzophenone and carbon dioxide, by permanganate in acetone solution to benzophenone and a little benzoic acid, and by nitric acid in glacial acetic acid solution to diphenylacetic acid. Concentrated nitric and sulphuric acids convert it into a mixture of nitro-compounds, m. p. (indefinite) 40–145°. Zinc and acetic acid, sodium and ethyl or amyl alcohol, and boiling hydriodic acid are practically without action on it. Fuming hydriodic acid and red phosphorus at 200–210° convert it partly into diphenylmethane. It reacts with magnesium ethyl iodide or magnesium phenyl bromide, but the products have not been completely identified. Under the action of bromine in cold carbon tetrachloride solution in the presence of sunlight or under light, it appears to yield a monobromo-derivative,  $C_{27}H_{21}OBr$ , n. p. about 78°.

It appears, therefore, impossible that dibenzhydryl ketone is an intermediate product in the transformation of barium diphenylacetate into tetraphenylallene.

H. W.

**α,α-Benzylidenediphenylacetone [Benzhydryl Styryl Ketone].** EDGAR RACK (Ber., 1923, 56, [B], 1130–1131).—The substance closely resembles dibenzhydryl ketone in its extreme stability (cf. Vorländer and Rack, preceding abstract).

*Benzhydryl styryl ketone*,  $CHPh:CH:CO:CHPh_2$ , pale yellow, prismatic crystals, m. p. 102–103°, is prepared by the addition of aqueous potassium hydroxide solution to a mixture of benzhydryl methyl ketone and benzaldehyde dissolved in alcohol. The corresponding *dibromide* crystallises in colourless needles, m. p. 147–150°. It is transformed by magnesium phenyl bromide in ethereal solution into *αα,δδ-tetraphenylbutane-β-one*,  $CHPh_2:CH_2:CO:CHPh_2$ , colourless, prismatic crystals, m. p. 89–91°.

*Benzhydryl p-methoxystyryl ketone* forms pale yellow crystals, m. p. 130–131°.

H. W.

**The Action of Sodium on ββ-Diphenylpropionic Ester.** D. VORLÄNDER, EDGAR RACK, and WALTER LEISTER (Ber., 1923, 56, [B], 1131–1135).—Methyl ββ-diphenylpropionate, m. p. 48°, or ethyl ββ-diphenylpropionate, b. p. 183–185°/15 mm., is converted by sodium in the presence of anhydrous ether at the atmospheric temperature into a mixture of *αα,γγ-tetraphenylhexane-γ-ol*

b b \*

$\delta$ -one,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , small, colourless prisms or needles, m. p. 147—148°, and  $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- $\gamma$ - $\delta$ -dione,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , short, yellow prisms, m. p. 188—189°, which are separated from one another by taking advantage of their widely differing solubilities in alcohol. The hexanol is converted into the diketone by treatment with nitric acid (d 1.4) on the steam-bath, whereas the reverse transformation is effected with fuming, aqueous hydriodic acid and red phosphorus. The diketone is oxidised by chromic and acetic acids mainly to  $\beta$ - $\delta$ -phenylpropionic acid. The hexanecolone gives an acetate, colourless, lustrous needles, m. p. 99°, and an oxime, small, colourless needles, m. p. 169°. The hexanedione yields a monoxime,  $\text{C}_{20}\text{H}_{27}\text{O}_2\text{N}$ , colourless rodlets or needles, m. p. 162° after softening at 158°, a dioxime,  $\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2$ , colourless, lustrous needles, m. p. 211—212° (decomp.), and a phenylsazone,  $\text{C}_{42}\text{H}_{38}\text{N}_4$ , pale yellow needles, m. p. 198—203°.  $\alpha\alpha\zeta\zeta$ -Tetraphenylhexane- $\gamma$ -ol, colourless needles, m. p. 139—141°, is prepared by the reduction of the keto-alcohol or the diketone with sodium and boiling amyl alcohol.  $\alpha\alpha\zeta\zeta$ -Tetraphenyl-n-hexane, colourless leaflets, m. p. 124—125°, is obtained from the keto-alcohol or the diketone by means of zinc dust and concentrated hydrochloric acid in the presence of acetic acid or from the keto-alcohol by the action of amalgamated zinc and concentrated hydrochloric acid. It could not be prepared by these methods from  $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- $\gamma$ -ol.

The action of sodium on  $\alpha$ - $\beta$ -diphenylpropionic ester does not yield a crystalline condensation product. H. W.

**$\beta$ -Phenylbenzylideneacetophenone [Phenyl Diphenylvinyl Ketone].** D. VORLÄNDER, JOHANNES OSTERBURG, and OTTO MEYER (*Ber.*, 1923, 56, [B], 1136—1144).—The experiments were undertaken with the object of obtaining tetraphenylallene,  $\text{CPh}_2\cdot\text{C}\cdot\text{CPh}_2$ , from a ditertiary alcohol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ . The action of magnesium phenyl bromide on an ethereal solution of dibenzoylmethane does not proceed beyond the stage which results in the formation of  $\beta$ -hydroxy- $\beta$ -diphenylpropionophenone,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{COPh}$ , colourless prisms, m. p. 119°, which is also obtained from methyl or ethyl malonate and magnesium phenyl bromide even when a large excess of the latter is employed. It is converted by potassium hydroxide solution into a mixture of benzophenone and acetophenone and by aqueous hydrochloric acid into phenyl diphenylvinyl ketone,  $\text{CPh}_2\cdot\text{CH}\cdot\text{COPh}$ , pale yellow prisms, m. p. 91°. The latter substance and several related compounds (tetraphenylpropylene, tetraphenylallene, etc.) exhibit the property of remaining viscous for weeks or months in the supercooled condition at the atmospheric temperature. They do not immediately solidify when seeded, although crystallisation can then be generally induced by a slight rise of temperature. It can also be caused by chemical agents. Thus the ketone remains as an oil when the solvent is removed from its ethereal solution, but crystallises if the ethereal solution is evaporated in contact with dilute sulphuric acid. Substances with unsymmetrical, branched

angular molecules appear particularly prone to remain liquid at the undercooled state.

Hydroxydiphenylpropiophenone is converted by phenylhydrazine in acetic acid solution into a substance,  $C_{27}H_{22}N_2$ , lustrous, yellow tablets, m. p.  $222-223^\circ$ ; the compound is derived from phenyl diphenylvinyl ketone, and appears to be a tetraphenylpyrazoline. Phenyl diphenylvinyl ketone appears to be converted by hydroxylamine into a normal *oxime*,  $C_{21}H_{17}ON$ , colourless, transparent tablets, m. p.  $146^\circ$ . With a molecular proportion of bromine in chloroform solution the ketone gives a *monobromo*-derivative,  $Ph_2CBrCOPh$ , prismatic crystals, m. p.  $168^\circ$  after softening at  $155^\circ$ . Reduction of the ketone with zinc dust and glacial acetic acid yields the *pinacone* of diphenylpropiophenone,  $C_{42}H_{38}O_2$ , colourless needles, m. p.  $192^\circ$ . The ketone does not react readily with hydrogen chloride, hydrogen bromide, or picric acid under widely varied conditions; with a saturated solution of hydrogen bromide in glacial acetic acid at  $100^\circ$ , it gives a *bromide*, pale yellow needles, m. p. (indefinite)  $135-137^\circ$ , which is possibly not homogeneous. It reacts with ethyl malonate in the presence of sodium ethoxide, but the product of the action has not been fully investigated. It does not appear to react with concentrated sulphuric acid. Phenyl styryl ketone, on the other hand, combines with sulphuric acid in the presence of benzene, giving a *compound*,  $C_{15}H_{12}O_2 \cdot 2H_2SO_4$ , whilst phenyl methoxystyryl ketone gives a similarly constituted *substance*, reddish-violet crystals.

Phenyl diphenylvinyl ketone is converted by magnesium phenyl bromide in the presence of ether into tetraphenylpropylene alcohol, which is smoothly transformed by boiling acetic anhydride into tetraphenylallene.

Benzylideneacetylacetone hydrochloride-*B* exhibits a pronounced tendency to the further addition of hydrogen chloride when it is very powerfully cooled. Benzylideneacetylacetone reacts in the usual manner with ethyl sodiomalonate, giving a monobasic acid, colourless crystals, m. p.  $128-130^\circ$ . Anisylideneacetylacetone readily yields a *hydrochloride*,  $C_{13}H_{15}O_3Cl$ , colourless, slender needles, m. p.  $48-50^\circ$ ; benzylidenebenzoylacetone reacts with hydrogen chloride, but the product could not be isolated. Ethyl sodiomalonate and benzylidenebenzoylacetone give the monobasic acid,  $C_{22}H_{20}O_5$ , m. p.  $54^\circ$ .

H. W.

**The Action of Benzene and Aluminium Chloride on  $\alpha\beta$ -Unsaturated Ketones and their Halogenated Derivatives.** D. ORLÄNDER and ALEXANDER FRIEDBERG (*Ber.*, 1923, 56, [B], 144-1150).—The action of benzene and aluminium chloride on a number of unsaturated diketones has been studied. The change appears to occur only with those compounds which unite readily with hydrogen chloride, and consists therefore in the substitution of the  $\beta$ -chlorine atom of the primarily formed hydrochloride by benzyl, and not in the addition of benzene at the  $\alpha\beta$ -unsaturated ring.

Phenyl styryl ketone, benzene, and aluminium chloride give

bb\*2

diphenylpropiofenone, m. p. 96°; resinous products are also formed and a portion of the unsaturated ketone is decomposed with production of acetophenone. The side reactions can be largely avoided by using phenyl styryl ketone hydrochloride in place of the ketone, or by a preliminary saturation of the solution of the latter in benzene with hydrogen chloride. Under similar conditions, phenyl *p*-methoxystyryl ketone remains unchanged. On the other hand, phenylanisylidenepropiofenone, m. p. 90°, is obtained from magnesium phenyl bromide and anisylidenacetophenone, which therefore resembles closely phenyl styryl ketone in its behaviour towards this reagent. Phenyl styryl ketone dibromide, benzene, and aluminium chloride yield  $\alpha\beta$ -triphenylpropiofenone,  $\text{CHPh}_2\text{-CHPh-COPh}$ , colourless needles, m. p. 182°, which is also obtained in a similar manner from bromodiphenylpropiofenone, m. p. 160–162°. Benzylidenementhone gives menthone and diphenylmethylmenthone,  $\text{C}_{10}\text{H}_{17}\text{O-CHPh}_2$ , m. p. 157°.

$\beta\beta$ -Diphenylpropiofenone is converted by hydrogen chloride in the presence of benzaldehyde to  $\beta\beta$ -diphenyl- $\alpha$ -benzylidenepropiofenone hydrochloride,  $\text{CHPh}_2\text{-CHBz-CHPhCl}$ , needles, m. p. 185°, from which the benzylidene group is removed by treatment with aluminium chloride and warm benzene.

The additive compound,  $\text{C}_{22}\text{H}_{18}\text{O}_3\text{S}$ , of phenyl styryl ketone and benzenesulphonic acid is obtained from its components in ethereal solution or when a solution of the ketone in benzene is saturated with sulphur dioxide and subsequently treated with aluminium chloride. If the latter reaction is prolonged the benzenesulphanyl residue is replaced by phenyl, thus yielding diphenylpropiofenone. Phenyl *p*-methoxystyryl ketone, benzene, sulphur dioxide, and aluminium chloride similarly yield the additive compound,  $\text{C}_{22}\text{H}_{20}\text{O}_4\text{S}$ , colourless crystals, m. p. about 177° (decomp.).

Distyryl ketone and benzenesulphonic acid give the product,  $\text{C}_{22}\text{H}_{20}\text{O}_3\text{S}$ , colourless needles, m. p. 168–170°, and 1:3-dibenzylidenecyclopentan-2-one gives the substance,  $\text{C}_{25}\text{H}_{23}\text{O}_3\text{S}$ , m. p. 155°; in neither case could the ketone be caused to combine with more than one molecular proportion of benzenesulphonic acid. H. W.

**The Additive Products of  $\alpha$ -Unsaturated Ketones and Mercury Halides.** D. VORLÄNDER and EGON EICHWALD (Ber., 1923, 56, [B], 1150–1152).—The additive compound of phenyl styryl ketone and mercuric chloride,  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{HgCl}_2$ , pale yellow needles, decomp. 92–93°, is obtained when a hot, concentrated solution of its components in alcohol is allowed to cool; it appears to have a limited ability to unite with hydrogen chloride. The compound from phenyl styryl ketone and mercuric bromide forms pale yellow, prismatic crystals, decomp. 88–90°. Phenyl *p*-methoxystyryl ketone mercuric chloride,  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{HgCl}_2$ , crystallises in pale yellow needles, decomp. about 114°, whereas the corresponding compound with mercuric bromide, pale yellow needles, decomposes at 115–117°. Di-*p*-methoxystyryl ketone mercuric chloride,  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{HgCl}_2$ , decomp. about 159°, is also described. H. W.

**The Velocity of Addition of Hydrogen Chloride to  $\alpha$ -Unsaturated Ketones.** D. VORLÄNDER and EGON EICHWALD (*Ber.*, 1923, 56, [B], 1153—1156).—The rate of combination of hydrogen chloride and certain  $\alpha$ -unsaturated diketones to form the so-called  $\beta$ -hydrochlorides has been measured in glacial acetic acid at 65°. Aliquot portions of the solution after definite intervals of time are poured into water and the combined acid in the precipitated mixture of ketone and ketone hydrochloride or the hydrochloric acid in the filtrate is estimated. Under suitable conditions, the additions take place in accordance with the law of mass action, and are catalytically accelerated by excess of hydrogen chloride. Since, however, the presence of the latter facilitates the dissociation of the additive compounds probably by altering the nature of the medium, the expected bimolecular course of the change has not been observed. In the presence of a large excess of hydrogen chloride, the reaction is of the first order. The velocity of addition of hydrogen chloride to phenyl styryl ketone dissolved in glacial acetic acid is eighteen times greater than that observed with anisylidenedibenzylketone, which exceeds that of benzylidenedeoxybenzoin.

In the case of acetophenone, the formation of a *B*-hydrochloride is facilitated by the introduction of a benzylidene residue, but hindered by an anisylidene group. In the case of dibenzyl ketone, on the other hand, the anisylidene derivative gives a very stable *B*-hydrochloride, whereas the benzylidene compound does not unite with hydrogen chloride to yield a *B*-salt. Conversely, the tendency to yield *A*-additive compounds preponderates in the case of the anisylidene derivative of acetophenone. It appears, therefore, that the readiness of formation of *A*-derivatives is paralleled by difficulty in the production of *B*-compounds and *vice versa*. H. W.

**Benzopyrylium Salts of Distyryl Ketones. II. Salts and Metallic Complexes of 4'-Dimethylamino-2-styrylbenzopyrylium.** JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (*T.*, 1923, 123, 1395—1404).

**The Mobility of Symmetrical Triad Systems. II. The Conditions Relating to Systems Terminated by the *o*-Phenylene Group. Derivatives of Indene.** CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (*T.*, 1923, 123, 1469—1509).

**A New Method of Preparing Dibenzoyl ethylene and Related Compounds.** JAMES B. CONANT and ROBERT E. LUTZ (*J. Amer. Chem. Soc.*, 1923, 45, 1303—1307).—*trans*-Dibenzoyl ethylene is prepared in 74% yield by gradually adding fumaryl chloride to a suspension of aluminium chloride in benzene, and decomposing the product by means of ice. The use of toluene in place of benzene leads to the formation of *trans*-ditoluoyl ethylene,  $C_6H_5(CO \cdot C_6H_4Me)_2$ , pale yellow needles, m. p. 148°, yield 75%; this is converted into *cis*-ditoluoyl ethylene, colourless needles, m. p. 123°, by the action of sunlight in acetone solution, the reverse change being effected by the action of iodine in chloroform solution. Either isomeride is reduced to ditoluoyl ethane by means of sodium hyposulphite in hot alcoholic solution, or by means of zinc and acetic acid. *trans*-Di-*p*-chlorobenzoyl ethylene, pale yellow crystals, m. p. 172°, is

formed by the gradual addition of aluminium chloride to a mixture of fumaryl chloride, carbon disulphide, and chlorobenzene, the whole being subsequently heated at 45–50° for two and a half hours and decomposed by means of ice, yield 51%. *cis*-*Di-p*-chlorobenzoyl ethylene, slender, white needles, m. p. 102°, is formed from the *trans*-isomeride in chloroform solution by the action of sunlight; the *trans*-form is reproduced in the presence of iodine. *Di-p*-chlorobenzoyl ethane, colourless crystals, m. p. 151°, is obtained by the reduction of the *cis*- or *trans*-form of the ethylene derivative, by means of sodium hyposulphite, or of zinc dust and acetic acid. *trans*-*Di*-(2:4:6-trimethylbenzoyl)ethylene, pale yellow crystals, m. p. 174°, is produced in 75% yield from fumaryl chloride, aluminium chloride, mesitylene, and carbon disulphide; when an alcoholic solution containing a slight amount of undissolved substance is exposed to sunlight in a quartz vessel, incomplete conversion occurs to *cis*-*di*-2:4:6-trimethylbenzoyl ethylene, colourless needles, m. p. 120°. Either the *cis*- or *trans*-isomeride is reduced to *di*-2:4:6-trimethylbenzoyl ethane, colourless crystals, m. p. 138.5°. *Di-p*-methoxybenzoyl ethylene has been obtained as a pale yellow solid, m. p. 165.5°, from fumaryl chloride, aluminium chloride, carbon disulphide, and anisole. The yield is poor, and so far, a colourless isomeride has not been prepared. W. S. N.

**Quinonemethides [Methylenequinones] and Pseudophenol halogenides.** HANS LINDEMANN (*Annalen*, 1923, 431, 276–300).—Although the pseudophenolhalogenides (*o*- or *p*-hydroxybenzyl halides) give acetates on treatment with acetyl chloride, they do not give salts by the action of alkali, but are converted into insoluble products. Zincke's explanation (*A.*, 1907, i, 322), that these compounds possess a semiquinonoid structure but are capable of reacting in the hydroxybenzenoid form, is insufficient, since an equilibrium between such forms would unquestionably be disturbed in the presence of alkali, with formation of the normal alkali salt. It is now suggested that actually a salt is first produced, but concurrently hydrogen halide is eliminated giving a quinonemethide (methylenequinone), which then undergoes polymerisation. The possibility of tautomerism is, of course, not excluded.

The existence of derivatives of methylenequinone, unsubstituted in the methylene group, has been questioned by Pummerer (*A.* 1915, i, 417), dimeric formulæ being assigned to these compounds. Nevertheless, whilst the polymerides of methylenequinones, not substituted in the methylene group, are yellow and dimeric, those derived from methylene substituted quinonemethides are colourless, and nearly always trimeric. This difference is unexplained by means of Pummerer's formulæ. In order, therefore, to obtain further evidence on the subject, methylenequinones containing halogen in the methylene group have been prepared from the corresponding *p*-hydroxybenzylidene halides, and their reactions investigated.

The benzylidene halide is prepared by the action of phosphorus pentahalide in benzene solution on the relevant aldehyde, into which it is reconverted by means of hot glacial acetic acid, or of

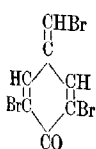
aqueous or alcoholic alkali. If the reaction with alkali is conducted in the cold, an unstable blue intermediate compound is formed; it is suggested that the change takes place through the quinone halogen methide. In prolonged contact with cold alcohol, or more rapidly in the boiling solution, the benzylidene halide is converted into the aldehyde. If, however, it is quickly dissolved in cold alcohol, or if an ethereal solution is shaken with aqueous sodium acetate, hydrogen halide is eliminated with formation of the quinonehalogenmethide, the reverse change being effected by means of hydrogen halide in glacial acetic acid solution. The action of hydrogen chloride on a quinonebromomethide gives *p*-hydroxybenzylidenechloridebromide, from which hydrogen bromide, not hydrogen chloride, is eliminated by the action of alcohol or sodium acetate.

The quinonehalogenmethides described are unimolecular, but polymerise somewhat readily, particularly in hot benzene solution. Moreover, they exhibit no tendency to form ethane derivatives (cf. Fries and Kann, A., 1907, i, 613), but are converted with extraordinary ease by means of aqueous alkali, or even hydroxylic solvents, into the original hydroxyaldehydes. The dimeric structure is therefore excluded for these quinonehalogenmethides.

During the reaction with alkali, a blue coloration appears, which may be due to an intermediate compound containing bivalent carbon. This is most readily observed when gaseous ammonia is led into a benzene solution of the halogenmethide, or of the benzalhalide; a blue precipitate is formed, which gradually changes into the yellow benzalimine. The latter immediately passes into the aldehyde in contact with warm dilute acid. The same anil is formed by the action of aniline on the halogenmethide, the benzalhalide, or the original aldehyde.

The action of warm acetic anhydride and concentrated sulphuric acid on 3:5-dibromo-4-hydroxybenzaldehyde gives the *triacetate*,  $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OAc})_2$  (I), m. p.  $125^\circ$ , which is converted by boiling with dilute hydrochloric acid and acetic acid into the *monoacetate*,  $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHO}$ , m. p.  $112^\circ$ . The solid *sodium* salt of the aldehyde reacts at  $100^\circ$  with dimethyl sulphate, giving 3:5-dibromo-4-methoxybenzaldehyde, white needles, m. p.  $82\text{--}86^\circ$ ; the latter is converted by warming with phosphorus pentabromide into 3:5-dibromo-4-methoxybenzylidene bromide, large, white leaflets, m. p.  $60\text{--}64^\circ$ . Incidentally, anisaldehyde is converted by treatment with bromine in glacial acetic acid solution into 3:5-dibromo-4-methoxybenzoic acid. The following compounds, the reactions of which are described above, have been obtained.

3:5-Dibromo-4-hydroxybenzylidene bromide, white needles, m. p.  $98\text{--}101.5^\circ$ , and its *acetate*, m. p.  $80^\circ$ . 3:5-Dibromo-quinonebromomethide (annexed formula), small, yellow needles, m. p.  $120^\circ$ . 3:5-Dibromo-4-hydroxybenzylidene chloride bromide,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHClBr}$ , white needles, m. p.  $70\text{--}74^\circ$ . 3:5-Dibromo-4-hydroxybenzylideneaniline, large, orange prisms, m. p.  $150\text{--}152^\circ$ . Unstable, yellow *imine* of 3:5-dibromo-4-hydroxybenzaldehyde. 2-Hydroxy-4:6-dimethylbenzaldehyde, large,



colourless, vitreous needles, m. p. 48°, is obtained as a by-product in the preparation of 4-hydroxy-2:6-dimethylbenzaldehyde by the action of hydrogen cyanide on xylenol in the presence of aluminium chloride. It is volatile in steam and gives a phenylhydrazone, m. p. 127°. 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzaldehyde, long, white needles, m. p. 181°, is obtained by the bromination of 4-hydroxy-2:6-dimethylbenzaldehyde in glacial acetic acid solution. It gives an acetate, large, white leaflets, m. p. 149°, and a triacetate, white needles, m. p. 114°. 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzylidene bromide, long, white needles, m. p. 154°, its acetate, white prisms, m. p. 152°, and its anil, white prisms, m. p. 212°. 3:5-Dibromo-2:6-dimethylquinonebromomethide, m. p. 200° (indefinite). 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzylidene chloride, white needles, m. p. 153°, does not depress the melting point of the corresponding bromide. 3:5-Dibromo-2:6-dimethylquinonechloromethide, pale yellow needles, m. p. 132°. 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzylidene chloride bromide, white needles, m. p. 151°, does not depress the melting point of the bromide or chloride, and gives an acetate, m. p. 138°.

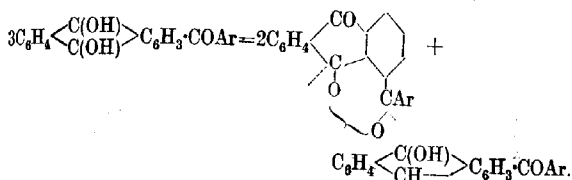
The author describes an apparatus (cf. Ziegler, A., 1921, i, 165) by means of which one litre of anhydrous hydrocyanic acid may be prepared in one hour.

W. S. N.

**Derivatives of  $\beta$ -Methylantraquinone. II. The Synthesis of Chrysophanic Acid.** [1:8-Dihydroxy-3-methylantraquinone.] R. EDER and C. WIDMER (*Helv. Chim. Acta*, 1923, 6, 419—424; cf. A., 1922, i, 260).—The condensation of  $\alpha$ -nitrophthalic acid with *m*-cresol in presence of aluminium chloride is much improved if a large excess of *m*-cresol is used instead of an indifferent solvent, and if the use of any alkali is avoided a 40% yield of 3-nitro-*o*-3'-hydroxy-*p*-toluoylbenzoic acid is obtained. Under the same conditions but using  $\alpha$ -nitrophthalic anhydride, the yield of the same product is practically theoretical. In a similar manner,  $\alpha$ -acetylaminophthalic anhydride can be condensed with *m*-cresol to give 3-amino-*o*-3'-hydroxy-*p*-toluoylbenzoic acid, and  $\alpha$ -hydroxyphthalic anhydride with *m*-cresol to give 3-hydroxy-*o*-3'-hydroxy-*p*-toluoylbenzoic acid; the yields are, however, comparatively poor. The above 3-amino-*o*-3'-hydroxy-*p*-toluoylbenzoic acid, when heated at 150° with concentrated sulphuric acid, is converted into 8-amino-1-hydroxy-3-methylantraquinone, lustrous, bronze needles, m. p. 245—246°. In boiling sodium hydroxide solution, it is sparingly soluble with a reddish-violet colour, and in concentrated sulphuric acid it dissolves with an orange-yellow colour. From a mixture of pyridine and water, it crystallises in violet-black needles containing pyridine. By diazotising in concentrated sulphuric acid and subsequent heating, it can be converted into chrysophanic acid. When 6-amino-*o*-3'-hydroxy-*p*-toluoylbenzoic acid is heated in sulphuric acid it forms 5-amino-1-hydroxy-3-methylantraquinone, bronze needles, m. p. 248—249°, which can also be diazotised and converted into the previously described 1:5-dihydroxy-3-methylantraquinone.

E. H. R.

**A New Class of Free Organic Radicles. III.** ROLAND SCHOLL and HERBERT HÄHLE (*Ber.*, 1923, 56, [B], 1065—1075; cf. A., 1921, i, 872; this vol., i, 584).—The only method of preparative importance for the production of the benzoyloxanthronyls has consisted hitherto in the reduction of 1-benzoylanthraquinones with metallic powders in the presence of concentrated sulphuric acid. This process, however, only leads readily to the isolation of homogeneous substances when the sulphates are insoluble or sparingly soluble in cold concentrated sulphuric acid. An alternative method is now described in which the 1-benzoylanthraquinones are reduced to the corresponding quinols, and the latter are converted by dehydrogenation and disproportioning into the required compounds in accordance with the scheme:



*p*-Chlorobenzoylanthraquinone is reduced by zinc dust and glacial acetic acid to *p*-chlorobenzoylanthraquinol under conditions which are very exactly described in the original, and the reddish-brown solution is poured into boiling concentrated hydrochloric acid which contains sodium chloride and a little potassium dichromate. A vigorous action is observed whereby the green oxonium chloride is produced. The mixture is poured into ammonia and the precipitated *p*-chlorobenzoyloxanthronyl is crystallised from acetic anhydride containing a little sodium acetate.

Protracted treatment with boiling acids causes the disproportioning of the benzoyloxanthronyls to benzoylanthraquinones and, probably, arylanthraquinonylcarbinols,  $\text{C}_6\text{H}_4\text{--}\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}\text{--}\text{C}_6\text{H}_3\text{--CHAr--OH}$ .

The photochemical disproportioning of *p*-chlorobenzoyloxanthronyl dissolved in nitrobenzene has been investigated further by titration with bromine solution. The change occurs very slowly at the atmospheric temperature in darkness, somewhat more rapidly in diffused daylight, and completely in about one and three-quarter hours in direct sunlight. In boiling solution, the change takes place fairly readily in diffused daylight.

The disproportioning of the benzoyloxanthronyls by acids, alkalis, or phosphorus trichloride is described; the course of the changes has not yet been elucidated definitely.

H. W.

**Ketocineole. V.** GUIDO CUSMANO (*Gazzetta*, 1923, 53, i, 95—200; cf. A., 1919, i, 212, 213; 1920, i, 346).—In spite of its relationship to ketoterpin, ketocineole exhibits the chemical behaviour, not of the monocyclic, but of the bicyclic, terpenic ketones, specially of camphor. It is now found that the  $\alpha$ -carbonylic

derivative of ketocineole, to which the name diketocineole is given, is a yellow compound behaving solely as a diketone and is hence closely analogous to camphorquinone.

*Oximinoketocineole* (annexed formula), prepared by the action of ethyl nitrite on ketocineole in presence of sodium or, better, of hydrochloric acid, forms large crystals (+H<sub>2</sub>O), m. p. about 90° or (anhydrous) 132°. When treated with phenylhydrazine, it yields *diketocineole oxime phenylhydrazone*, C<sub>16</sub>H<sub>21</sub>ON<sub>3</sub>, which forms pale yellow crystals, m. p. 186°. *Diketocineole dioxime*, C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>N<sub>2</sub>, separates in minute crystals, m. p. 195° (decomp.), and, when dissolved in ether containing nitrous fumes gives, not the diketone, but the *anhydride* of the dioxime or *furazan*, C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>, which forms lozenge-shaped crystals, m. p. 89°.

*Diketocineole* (annexed formula), obtained by heating oximinoketocineole in acetic acid solution with sodium hydrogen sulphite and decomposing the resulting compound with dilute hydrochloric or sulphuric acid, forms colourless crystals (+H<sub>2</sub>O) with a rhombic base and becomes yellow and volatile when dehydrated in a vacuum over sulphuric acid. It reduces neither Fehling's solution nor ammoniacal silver nitrate solution, and gives no coloration with ferric chloride. When oxidised with 2% permanganate solution, it gives a good yield of cineolic acid,  $\begin{array}{c} \text{CH}_2\text{---CMe}(\text{CO}_2\text{H})\text{---O} \\ | \\ \text{CH}_2\text{---CH}(\text{CO}_2\text{H})\text{---CMe}_2 \end{array}$ .

T. H. P.

**Homologues of Camphor. II.  $\beta$ -Methylcamphene and  $\beta$ -Methylcamphenilone.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 139—144).—6-Methylisoborneol (cf. this vol., i, 588) when heated with potassium hydrogen sulphate, loses water, yielding  $\alpha$ - and  $\beta$ -methylcamphenes, principally the latter.  $\beta$ -Methylcamphene, b. p. 170—170.5°/760 mm., m. p. 98—100°, when warmed with glacial acetic acid yields acetyl-6-methylisoborneol, which on hydrolysis gives the corresponding alcohol.  $\beta$ -Methylcamphene, on treatment with oxides of nitrogen and subsequent warming with alcoholic potash, yields  $\beta$ -methylcamphenilone, m. p. 141—142°, the *semicarbazone*, m. p. 231—232° (decomposition), of which is prepared. The action of sodamide on  $\beta$ -methylcamphenilone is to yield the *amide* of  $\beta$ -methylcamphenylic acid, C<sub>10</sub>H<sub>19</sub>ON, m. p. 124—125°.

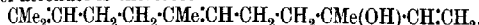
R. T.

**Homologues of Camphor. III. Tertiary Methylbornyl Alcohol and its Dehydration.** S. S. NAMETKIN and M. A. SCHLESINGER (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 144—147; cf. preceding abstract).—Tertiary methylbornyl alcohol easily loses water, yielding, not methylfenchene, as might be expected, but  $\alpha$ -methylcamphene, which was previously obtained by the dehydration of tertiary methylisobornyl alcohol.

R. T.

**The Conversion of Carvone into Carvacrol.** FRIEDRICH LICHTER (*Chem. Ztg.*, 1923, 47, 489).—*d*-Carvone was heated for five hours at 205° and, after cooling, the carvacrol estimated by extraction with 5% potassium hydroxide. The quantity of carvacrol formed was inappreciable. This observation is in agreement with that of Baeyer (A., 1894, i, 297), who found that carvone remains unchanged when boiled for one hour, whilst eucarvone, under similar conditions, undergoes complete transformation, and contrary to that of Dormaar (A., 1905, i, 222), according to whom carvone, when heated at 205° for five hours, undergoes 36% transformation and eucarvone only 21%. W. T. K. B.

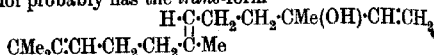
**Higher Terpene Compounds. VIII. The Constitution of Nerolidol (Peruvicol).** L. RUZICKA (*Helv. Chim. Acta*, 1923, 6, 33—492).—A comparison of the physical and chemical properties of the aliphatic sesquiterpene derivatives farnesol and nerolidol, on the one hand, with those of geraniol and linalool, on the other, suggests that nerolidol bears the same relation to farnesol as linalool does to geraniol. The hydroxyl group of geraniol and farnesol is far more reactive than that of linalool and nerolidol. These considerations suggest that nerolidol, like linalool, is a tertiary alcohol, and its molecular refraction indicates the presence of three double bonds, but not of conjugated double bonds. The probable constitution of nerolidol is therefore



In confirmation of this reasoning, it is found that nerolidol is oxidised by chromic acid to farnisal, just as linalool is oxidised to citral, and by the action of acetic anhydride on nerolidol it is converted into farnesol, just as linalool is converted into geraniol. The hydrolysed product of the action of acetic anhydride on nerolidol gave on distillation three fractions. The first fraction consisted principally of sesquiterpenes, a considerable proportion of which consisted of farnesene; the second consisted of unaltered nerolidol, and the third contained the farnesol, which was identified by its enicarbazone [cf. *J.S.C.I.*, 1923, July]. E. H. R.

**Higher Terpene Compounds. IX. The Complete Synthesis of *dl*-Nerolidol and Farnesol.** L. RUZICKA (*Helv. Chim. Acta*, 1923, 6, 492—502; cf. preceding abstract).—The synthesis of *dl*-nerolidol was accomplished in the following manner.  $\beta$ -Dihydro- $\psi$ -jonone,  $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}$ , was condensed with acetylene and sodamide, giving in almost quantitative yield *homogeranyl-ethynylmethylcarbinol*, or *dehydro-*dl*-nerolidol*,  $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CH}$ . This is a colourless oil with a faint odour, b. p. 146—147°/12 mm.,  $n_D^{20}$  0.8908,  $n_D^{25}$  1.4789. Its phenylurethane could not be crystallised. By reduction with sodium in ether solution, this gave *dl*-nerolidol, a colourless oil with a pleasant odour, b. p. 145—146°/12 mm.,  $n_D^{20}$  0.8908,  $n_D^{25}$  1.4789. Its phenylurethane could not be crystallised. By reduction with sodium in ether solution, this gave *dl*-nerolidol, a colourless oil with a pleasant odour, b. p. 145—146°/12 mm.,  $n_D^{20}$  0.8908,  $n_D^{25}$  1.4789. This did not give a crystalline phenyl- or naphthyl-urethane. It was identified by conversion by acetic anhydride into farnesol (cf. preceding abstract). *cis*- and *trans*-form of nerolidol is possible, and four stereoisomeric

forms of farnesol. Whilst the densities of natural and synthetic nerolidols are the same, farnesols of different origins differ considerably. If, as has been suggested, geraniol is a *trans*-form, then since the above synthesis starts from geraniol, the synthetic *dl*-nerolidol probably has the *trans*-form



and the farnesol prepared from it has either a *trans*-*cis*- or a *trans*-*trans*-form, or is more probably a mixture of the two, just as a mixture of geraniol and nerol is formed by the action of acetic anhydride on linalool.

When farnesol is heated at 170° and 12 mm. with potassium hydrogen sulphate, a sesquiterpene distils over, b. p. 128—130°/12 mm.,  $d_4^{20}$  0.8385,  $n_D^{20}$  1.4965, which from its molecular refraction is taken to be farnesene. Its constants agree with those of the aliphatic sesquiterpene found by Semmler and Spornitz in Java citronella oil (A., 1914, i, 193). When this farnesene is heated at 140° with 90% formic acid it is converted into a monocyclic sesquiterpene, b. p. 126—128°/12 mm.,  $d_4^{20}$  0.8776,  $n_D^{20}$  1.4961. It appears to be the same product as that obtained from nerolidol in the same manner.

Geranyl chloride can be obtained by the action of phosphorus pentachloride on geraniol in light petroleum, but is best prepared on a large scale with phosphorus trichloride by the method of Tiemann and Schmidt (A., 1896, i, 382). E. H. R.

**Pinane.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 147—151).—Pinene on reduction by the Sabatier-Senderens process (Zielinski, *Ber.*, 1911, 44, 2782) gave a mixture of hydrocarbons not possessing the pinene structure, principally isobornylane. This work is repeated at a lower temperature (155—158° instead of 180°), when a product, b. p. 155—156°,  $d_4^{20}$  0.8606,  $n_{20}$  1.4669,  $[\alpha]_D$  —42.38°, is obtained, which is probably *pinane*,  $\text{C}_{10}\text{H}_{18}$ , as its refractive index corresponds with the presence of the pinene ring. It does not react with nitric acid, *d* 1.4, even on warming; with bromine it slowly evolves hydrogen bromide. *Nitropinane*,  $\text{C}_{10}\text{H}_{17}\text{NO}_2$ , b. p. 134—135°/23 mm.,  $d_4^{20}$  1.0416,  $n_{20}$  1.4814, was prepared and appears also to possess the pinene structure. R. T.

**Fenchylene.** II. S. S. NAMETKIN and (MLLE) A. K. RUSHENCEVA (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 152—156; cf. *ibid.*, 1916, 48, 450).—Two amides of xanthylisofenchyl alcohol,  $\text{C}_{10}\text{H}_{17}\text{O}-\text{C}-\text{S}-\text{NH}_2$ , one m. p. 69—70°,  $d_4^{20}$  0.8134,  $[\alpha]_D$  —37.77°, and the other an oil, are obtained by the action of 10% ammonia on the corresponding methyl or ethyl esters. The solid amide gives on hydrolysis pure isofenchyl alcohol, m. p. 60—61°,  $[\alpha]_D$  —27.04° in alcoholic solution,  $d_4^{20}$  0.8037; both amides on heating at 180° yield fenchylene; that from the crystalline amide has b. p. 140—141°/740 mm.,  $d_4^{20}$  0.8397,  $n_{20}$  1.4502,  $[\alpha]_D$  —57.28°, the *nitroethyl chloride*, m. p. 131°, of which yields fenchylcamphoric acid on oxidation. The fenchylene obtained from the liquid amide has

p. 140.5—141°/760 mm.,  $d_{20}^{20}$  0.8398,  $n_{20}^{20}$  1.4505,  $[\alpha]_D -50.98^\circ$ , and probably contaminated with cyclofenchene. R. T.

**Constituents of some Indian Essential Oils. VIII. The Essential Oil from the Gum-oleo-resin of *Boswellia serrata* Roxb.** JOHN LIONEL SIMONSEN (*Indian For. Rec.*, 1923, 9, 89—306).—This oil does not consist of *d*- $\alpha$ -pinene and  $\beta$ -pinene as stated by Pearson and Puran Singh (*Indian For. Rec.*, 1918, 6, 303), but is mainly *d*- $\alpha$ -thujene, containing a little  $\alpha$ -pinene and probably a little *d*- $\alpha$ -phellandrene, but no  $\beta$ -pinene. The thujene was characterised by conversion into *d*- $\alpha$ -thujaketonic acid [mixed with  $\alpha$ -thujaketonic acid, identified as the semicarbazone, m. p. 197° cf. Thomson, T., 1910, 97, 1511], *l*- $\alpha$ -thujadicarboxylic acid, *d*-thujaketonic acid (oxime, m. p. 111—112° [cf. Wallach, A., 1893, 105]); semicarbazone, m. p. 195—196° [cf. Seyler, A., 1902, i, 229] and  $\beta$ -thujadicarboxylic acid.

The purified *d*- $\alpha$ -thujene had b. p. 152—152.5°/699 mm.,  $d_{20}^{20}$  0.8314,  $n_{20}^{20}$  1.4502, and  $[\alpha]_D^{20} +37.69^\circ$  (after two months,  $[\alpha]_D^{20} +37.13^\circ$  [cf. Fowler and Malandkar, *J. Ind. Inst. Sci.*, IV, 27]). E. E. T.

**The Essential Oils of Two Species of *Homoranthus* and the Occurrence of Ocimene.** A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1923, 14, 145—148).—*Homoranthus virgatus*, a slender, upright shrub growing in New South Wales and Queensland, contains an average of 0.7% of essential oil, having the following characters:  $d_{15}^{15}$  0.8660,  $\alpha +28^\circ$ ,  $n_{20}^{20}$  1.4743, saponification value 6.16 before, and 27.65 after acetylation. It contains about 80% of *d*- $\alpha$ -pinene, and the remainder consists of a sesquiterpene, b. p. 129—132°/10 mm.,  $d_{15}^{15}$  0.9171,  $n_{20}^{20}$  1.5049, together with small amounts of amyl alcohol, isovaleraldehyde, and a paraffin, m. p. 65—66°. The essential oil of *H. flavescens*, on the other hand, contains about 90% of the olefinic terpene ocimene, together with *d*- $\alpha$ -pinene, sesquiterpene, and the minor constituents mentioned above. The oil has the following characters:  $d_{15}^{15}$  0.8429,  $\alpha -1.75^\circ$ ,  $n_{20}^{20}$  1.4836, saponification value after acetylation 51—85. The high alcohol and ester numbers are not due to the presence of actual ester and alcohol, but to some resinous substances which appear to increase in amount soon after the distillation of the oil. G. F. M.

**Aggregation and Disaggregation. Hydrolysis of Shellac Resin. Hydrogenation of Caoutchouc.** C. HARRIES (*Ber.*, 1923, 56, [B], 1048—1051).—The terms "polymerisation" and "depolymerisation" are frequently applied to alterations in the state of aggregation of colloids. Since, however, these expressions have a definite meaning in organic chemistry and denote a type of change which is probably not identical with that observed in the case of colloids, it is proposed that they should be replaced in connexion with the latter by the terms "aggregation" and "disaggregation."

In a recent communication, Harries and Nagel (this vol., i, 120) have described two forms of purified shellac resin one of which is soluble in alcohol and readily hydrolysed, whereas the other is

insoluble in alcohol and only hydrolysed with great difficulty. The products, however, appear to be structurally identical and differentiated only by difference in the state of aggregation. The unreactive can be transformed into the active variety by solution in glacial acetic or, preferably, formic acid and reprecipitation by water, whilst the reverse change can be effected by treatment with ether containing a little hydrogen chloride. It is supposed that the inability of one product to enter into chemical change is due to the mechanical arrangement of the particles in such a manner that an inadequate point of attack is offered to a reagent.

Many unsuccessful attempts have been made to hydrogenate caoutchouc catalytically and this has been effected by Pummerer and Burkard (this vol., i, 49) and by the author by the use of highly purified material in very dilute solution. If, however, crude caoutchouc is first rendered highly plastic mechanically, it can be subsequently hydrogenated to perhydrocaoutchouc at the atmospheric temperature in the presence of light petroleum under a pressure of a few atmospheres. The product behaves as saturated towards bromine; it becomes decomposed at 220–230°. It appears, therefore, that the ability of caoutchouc to unite with hydrogen depends directly on its degree of dispersion or aggregation.

It is suggested that the vulcanisation of rubber is due to a displacement of the aggregation. H. W.

**Rutin, Sophorin, and the Sugar which they yield on Hydrolysis.** H. TER MEULEN (*Rec. trav. chim.*, 1923, 42, 380–386).—Rutin, prepared from the dried leaves of *Ruta graveolens*, was hydrolysed in glycerol solution by a solution of rhamninase obtained from *Rhamnus infectoria*, the results, as shown by a series of control experiments, indicating that the sugar of the glucoside is rhamninose. Evidence is adduced, based on the work of Wachs (A., 1894, i, 299), of Zwenger and Dronke (*Annalen*, 1862, 123, 145), and of the present author, to show that sophorin and rutin are identical, the formula being  $C_{33}H_{42}O_{20} \cdot 4H_2O$ . Attempts to obtain crystalline rhamninose from the glucoside were unsuccessful. No enzyme present in *Ruta graveolens* or *Sophora japonica* hydrolyses rutin, but seeds of *Rhamnus cathartica* contain a substance which may be used as a substitute for rhamninase. H. J. E.

**Synthesis of *m*-Nitrotolyl-glucoside and the Disinfecting Value of *m*-Nitrocresol.** E. GLASER and H. PRÜFER (*Biochem. Z.*, 1923, 137, 429–438).—3-Nitro-*p*-tolylglucoside tetra-acetate was prepared from 3-nitro-*p*-cresol and  $\beta$ -acetobromoglucose. It melts at 201–203° and has  $[\alpha]_D +26.8^\circ$  in chloroform. It was hydrolysed in methyl-alcoholic solution by dry ammonia. 3-Nitro-*p*-tolylglucoside melts at 128–129° and has  $[\alpha]_D -77.5^\circ$  in water. Emulsin effects partial hydrolysis. 3-Nitro-*p*-cresol is six times as powerful a disinfectant as phenol when tested on *Staphylococcus pyogenes citreus*. The glucoside has no disinfectant action in vitro, but is readily hydrolysed by *Staphylococcus*, the dextrose acting as a growth promoter. H. K.

**The Constitution of Cantharidin.** SAMUEL COFFEY (*Rec. trav. chim.*, 1923, 42, 387—436; cf. Gadamer, A., 1915, i, 432).—A consideration of Gadamer's review of the subject (A., 1914, i, 707) together with work subsequently published (Auwers, A., 1913, i, 1319; Danckwort, A., 1915, i, 432, 433; Gadamer, A., 1915, i, 432; 1917, i, 659, 704; 1920, i, 859; Haworth, T., 1913, 103, 1242; Rudolf, A., 1917, i, 468) leads to the general conclusion that one of the three formulæ considered possible by Gadamer for cantharidin is correct, although there appears to be insufficient evidence for accepting any particular formula in preference to the other two. An attempt was therefore made to prepare synthetically the three substances which, according to deductions from Gadamer's three formulæ, are the three possible deoxycantharidins viz., (a) *cis*-cyclohexane-1:2-diacetic anhydride, (b) *cis*-1:2-dimethylcyclohexane-4:5-dicarboxylic anhydride, (c) *cis*-1:2-dimethylcyclohexane-1:2-dicarboxylic anhydride.

The first-named substance was prepared by Leroux (*Ann. chim. phys.*, 1910, [viii], 21, 458), but only in small amount. As some quantity of this acid was required, the action of ethyl sodiomalonate on dibromocyclohexene was studied and found to take two courses, one yielding hexahydroisocoumaranone, the other cyclohexene and ethyl ethanetetra-carboxylate. The last-named substance behaves towards hydrazine as a normal ester (cf. Salomon and Pohl, A., 1895, i, 508). It was anticipated that ethyl sodiomalonate and the cyclohexenenchalogenohydrins would yield hexahydroisocoumaranone in quantity, but the results were poor owing to the large proportion of useless by-products, and the preparation of this substance was found to be most satisfactorily effected from ethyl sodiomalonate and cyclohexene oxide. It was not possible, however, to prepare 1:2-cyclohexenediacetic acid from it, and therefore attempts were made to prepare and reduce *o*-phenylenediacetic acid, the method of Moore and Thorpe (T., 1908, 93, 165) being found the most suitable. The acid is unaffected by treatment with sodium and either ethyl or amyl alcohol, but is quantitatively reduced to a mixture of *cis*- and *trans*-cyclohexanedi-acetic acids by means of platinum black and hydrogen. The separation of these acids was effected by very slow crystallisation from water or ethyl acetate and the *cis*-form was eventually obtained pure. On distillation, it yielded the anhydride, but this is a somewhat unstable substance. The acid and anhydride are not identical with deoxycantharidic acid and deoxycantharidin, respectively, as the m. p. of the pure acid is 162—163°, whilst that of deoxycantharidinic acid is 160—165°, and the silver salts crystallise with  $\frac{1}{2}$ H<sub>2</sub>O and 2H<sub>2</sub>O, respectively. Further, the two acids behave very differently on distillation with steam. Attention was therefore directed to the preparation of *cis*-1:2-dimethylcyclohexane-4:5-dicarboxylic acid. A substance to which the constitution of 4:5-dimethylphthalic acid was attributed was described by von Korzynski (A., 1902, i, 274), but a repetition of that worker's experiments showed that the acid prepared by him was not a dimethylphthalic acid, but a dimethylisophthalic acid identical with the acid that

may be obtained directly by the oxidation of durene. 4:5-Di-methylphthalic acid was thus apparently unknown, and attempts were made to prepare it. For this purpose, 4:5-dibromo-*o*-xylene and 4:5-dibromophthalic acid were used, but no successful result was obtained. *p*-Xylic acid was then used as a starting-point, this was heated with mercuric acetate, giving a mixture of the anhydrides of the two possible *o*-hydroxymercuri-*p*-xylic acids. These were treated with fuming sulphuric acid, and converted into the corresponding *o*-sulpho-*p*-xylic acids, which were purified by the fractional crystallisation of their barium and finally of their sodium salts. The orientation of these acids was demonstrated to be of the ortho-type by treatment with bromine water, which resulted in the elimination of carbon dioxide and the sulphonio group with formation of known dibromo-*o*-xylenes. On fusing the sodium salt of 5-sulpho-*p*-xylic acid with sodium formate, 4:5-dimethylphthalic acid was obtained. Attempts to reduce this acid to the corresponding hexahydro-derivative have as yet been unsuccessful.

In the course of the above work, the following substances, hitherto not described, have been prepared: The lactone of 2-cyclo-

hexanol-2-malonic acid,  $\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CO}_2\text{H})\text{CO}_2\text{H}$ , a pale yellow,  $\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{O} > \text{CO})$

viscous oil, not obtained crystalline, b. p. 190—200°/10 mm. (decomp.); ethyl cyclohexanol-2-malonhydrazide,

$\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , silky needles, m. p. 184—185° (corr. decomp.); cyclohexanol-2-malonamide,  $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$ , a white, granular, crystalline substance, m. p. 227—228° (corr. decomp.); cyclohexanol-2-malonohydrazide,

$\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$ , a white, crystalline powder, m. p. 226—227° (corr.); hexahydroisocoumaranone (cyclohexanolacetolactone),  $\text{C}_8\text{H}_{12}\text{O}_3$ , a colourless, mobile liquid of characteristic odour, b. p. 152—153°/28 mm., 138—139°/15 mm., 262.5—263.5°/765 mm.,  $d_4^{25}$  1.0925,  $n_D^{25}$  1.4790, m. p. —5.5°; cyclohexan-2-ol-1-acetic acid,  $\text{C}_8\text{H}_{14}\text{O}_3$ , crystals, m. p. 97—102°, silver and potassium salts of the acid, the latter crystallising in lustrous plates; cyclohexan-2-ol-1-acetamide,  $\text{C}_8\text{H}_{15}\text{O}_2\text{N}$ , large, characteristic clusters of prisms, m. p. 154° (corr.); cyclohexanolacetohydrazide,  $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$ , silky needles, m. p. 167.5° (corr.); cyclohexanolacetobenzohydrazide,  $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , colourless, feathery needles, m. p. 173—174° (corr.); cyclohexanolacetophenylhydrazide,  $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2$ , small, colourless crystals, m. p. 165.5° (corr.); dihydronaphthalenemono-ozonide, a colourless, amorphous, gummy solid, which explodes on heating to a fairly high temperature; *o*-phenylenediacetic acid monoamide,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ , small, brilliant needles, m. p. 207—208° (corr.); 3:4:3':4'-tetramethylbenzil (4:4-*o*-xylyl),  $\text{C}_{18}\text{H}_{18}\text{O}_2$ , a citron-yellow solid, m. p. 128.5° (corr.); yielding a golden-yellow, crystalline osazone, m. p. 199—200° (corr.); 2:3-di-*o*-4'-xylylquinoxaline,  $\text{C}_{24}\text{H}_{22}\text{N}_2$ , colourless needles, m. p. 158° (corr.); 4:5-dimethylphthalic anhydride,  $\text{C}_{10}\text{H}_8\text{O}_3$ , characteristic, square leaves, m. p. 208.5° (corr.); 4:5-dimethylphthalic acid,  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , long, colourless needles, m. p. 209° with evolution of water vapour.

2-Dibromocyclohexane has b. p. 97—98°/10 mm., 124—125°/36 mm., m. p. —6.0°,  $d_{4}^{20}$  1.7917,  $d_{16}^{20}$  1.7898,  $n_D^{20}$  1.5540. H. J. E.

**Tannins and Similar Substances. XIII. Stereoisomeric catechins. III.** KARL FREUDENBERG and LUDWIG PURDMANN *Ber.*, 1923, 56, [B], 1185—1194.—Four members of the catechin family have been isolated previously, viz., *d*- and *dl*-catechin and *d*- and *dl*-epicatechin. Kostanecki's Gambier catechin is pure *d*-catechin, which is convertible into a mixture of catechins from which *dl*-catechin can be isolated. The latter substance is the main component of Pega catechu (*acacatechin*) which contains also *l*-catechin. The isolation of the latter is now described and the relationships of the *d*-, *l*-, and *dl*-forms is firmly established. Further, it has been found possible to separate *d*-epicatechin in the homogeneous state from the products of the transformation of *d*-catechin and thence to place beyond doubt the racemic nature of *dl*-epicatechin. It is considered most probable that the epicatechin is derived from the catechin series by change in the arrangement of the groups attached to the two asymmetric carbon atoms, which occurs at appreciably different rates; a displacement of the ring is not involved.

The separation of *l*- and *dl*-catechins and *l*- and *dl*-epicatechins from the ethereal extract of *Acacia catechu* is described in detail, the compounds being obtained in the relative amounts: 60 : 320 : 30 : 30. Two specimens of *Acacia catechu* from India consisted respectively of nearly homogeneous *dl*-catechin and of a mixture of approximately equal amounts of *dl*- and *l*-catechins. A specimen of *Gambier catechu* yielded mainly *d*-catechin with minor quantities of the *dl*-derivative.

The transformation of *d*-catechin is effected conveniently in aqueous solution at 125°, the products being *dl*-catechin and *dl*- and *d*-epicatechins.

The following compounds are described in detail: *l*-Catechin,  $C_{15}H_{14}O_6 \cdot 4H_2O$ , m. p. (hydrated) 93—97°, (anhydrous) 174—175°, [indefinite]  $[\alpha]_{D}^{20}$  yellow —16.7° in aqueous acetone (50%), inactive in alcoholic solution: *l*-Catechin *penta-acetate*, m. p. 132°  $[\alpha]_{D}^{20}$  yellow —39.4° in tetrachloroethane: *Tetramethyl-l-catechin*, colourless crystals, m. p. 142—143°,  $[\alpha]_{D}^{20}$  yellow +12.0° ( $\pm 2^\circ$ ): *dl*-Catechin, colourless needles, m. p. 214—216° after previous softening. *dl*-Catechin *penta-acetate*, m. p. 166°. *l*-Epicatechin ( $+4H_2O$ ), m. p. 245° (corr. decomp.),  $[\alpha]_{D}^{20}$  yellow —68° in alcohol, —60° in aqueous acetone (50%). *l*-Epicatechin *penta-acetate*, colourless needles, m. p. 153—154°,  $[\alpha]_{D}^{20}$  yellow —15° when dissolved in *s*-tetrachloroethane. *Tetramethyl-l-epicatechin*, broad prisms, m. p. 153—154°,  $[\alpha]_{D}^{20}$  yellow —61.5° in *s*-tetrachloroethane. *d*-Epicatechin, m. p. 245° (decomp.),  $[\alpha]_{D}^{20}$  yellow +69° in alcohol (96%). *d*-Epicatechin *penta-acetate* ( $+4H_2O$ ), m. p. 153°,  $[\alpha]_{D}^{20}$  yellow +16°. *Tetramethyl-d-epicatechin*, m. p. 153°,  $[\alpha]_{D}^{20}$  yellow +60.9° when dissolved in *s*-tetrachloroethane. *dl*-Epicatechin crystallises in two forms, thick, glistening plates or slender needles, which probably contain differing proportions of water of crystallisation; it

has m. p. (anhydrous), 229—232°. *dl*-Epicatechin penta-acetate has m. p. 167°.

The presence of *l*- or *dl*-catechins causes an exaltation of the specific rotation of *l*-epicatechin, whereas *d*-catechin does not appear to be influenced by the presence of the epi modification.

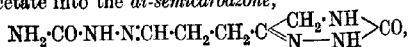
H. W.

**The Fission of Furfuryl Alcohol and the Mechanism of the Production of Lævulic Acid from Hexoses.** RUDOLF PUMMERER and WILHELM GUMP (*Ber.*, 1923, 56, [B], 999—1008).—Furfuryl alcohol is decomposed by hot, very dilute, methyl-alcoholic hydrogen chloride into methyl lævulate and a derivative of  $\delta$ -hydroxy- $\gamma$ -ketovaleraldehyde, the yield of unresinified products under these conditions being about 30—40% of the weight of the initial material. It has not been found possible to isolate  $\delta$ -hydroxy-lævulaldehyde in substance, but it is shown that the compound, when treated with boiling mineral acids, undergoes a remarkable intramolecular Cannizzaro reaction which results in the formation of lævulic acid.

5-Hydroxymethylfurfuraldehyde,  $\begin{array}{c} \text{CH}_2\text{C}(\text{CH}_2\text{-OH}) \\ \text{CH}=\text{C}(\text{CHO}) \end{array} > \text{O}$ , has been

shown previously to be an intermediate product in the conversion of hexoses into lævulic acid, but the further course of the reaction has not been elucidated hitherto. The present experiments make it appear probable that the next step in the series consists in the formation of  $\delta$ -hydroxylævulaldehyde, the aldehydic group being hydrolytically eliminated as formic acid. It is improbable that hydrolysis occurs previous to the rupture of the furan ring, since, in this case, furfuryl alcohol would be produced which, when treated with boiling mineral acids under the customary experimental conditions, yields only 5—40% of lævulic acid (the remainder of the alcohol becomes resinified) whereas 5-hydroxymethylfurfuraldehyde gives an approximately quantitative yield of formic acid and lævulic acid. It is therefore likely that the hydroxymethyl compound is transformed into the hydroxydiketoaldehyde,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CHO}$ , which is subsequently hydrolysed.

Furfuryl alcohol is converted by a boiling solution (0.1%) of hydrogen chloride in methyl alcohol into methyl lævulate, b. p. 85—86°/14 mm. (*p*-nitrophenylhydrazone, m. p. 136°; semicarbazone, lustrous leaflets, m. p. 148—149°), and  $\delta$ -methoxylævulaldehyde dimethyl acetal,  $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})_2$ , a colourless liquid, b. p. 97—98°/13 mm.,  $d_4^{20}$  1.0323,  $n_D^{20}$  1.4281, the constitution of which is established by its production from furfuryl methyl ether. It is converted by semicarbazide hydrochloride and sodium acetate into the *di*-semicarbazone,



thin, pale yellow leaflets, m. p. 222°, and by *p*-nitrophenylhydrazine in acetic acid solution (50%) into the *p*-nitrophenylhydrazone,  $\text{C}_{28}\text{H}_{27}\text{O}_4\text{N}_9$ , m. p. 216—217°. A second *p*-nitrophenylhydrazone,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}_3$ , is also obtained when the acetal reacts with *p*-nitro-

phenylhydrazine in the presence of dilute aqueous mineral acid. The acetal is converted by boiling 0.5N aqueous hydrochloric acid to levulinic acid and by methyl-alcoholic hydrogen chloride (2N) to methyl levulinate.

H. W.

#### Blue Dye from Furfuraldehyde and Diethylaniline.

PASCHKE (*Cellulosechemie*, 1923, 4, 32—33).—The green colouring matters of the malachite-green type which are formed by the condensation of furfuraldehyde with dimethyl- or diethyl-aniline in the presence of oxalic acid are relatively unstable. If, however, the green mass obtained by condensation with diethylaniline is boiled for a short time with alcoholic hydrogen chloride, the green colour is discharged, owing apparently to the rupture of the oxygen bridge of the furan ring. The brown solution is filtered cold, mixed with sodium chloride solution, then acidified with acetic acid and treated with ferric chloride solution drop by drop. A blue dye is thus formed which is separated by salting out and purified by solution in glacial acetic acid; its composition corresponds with the formula  $C_{25}H_{34}O_{10}N_2Cl_2$ . This dye contains more oxygen than would be present if the reaction were confined to a simple rupture of the furan ring, and its behaviour suggests the presence of phenolic hydroxyl groups. It has the properties of an acid dye, having a strong direct affinity for silk in an acid bath and dyeing cotton only as a mordant dye. The mordant lakes are extremely fast.

J. F. B.

#### Pyrylium Compounds. XII. The Constitution of Methyl-diphenylpyrylium Salts.

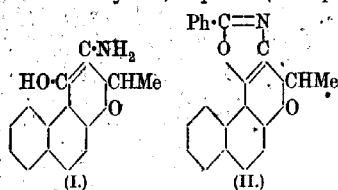
W. DILTNEY and J. FISCHER (*Ber.*, 1923, 56, [B], 1012—1013).—It has been pointed out recently by Schneider and Ross (*A.*, 1922, i, 1171) that the compounds described by Diltney as 2 : 6-diphenyl-4-methylpyrylium salts can be obtained from dypnone and differ from those derived from phenyl propenyl ketone and acetophenone; they are therefore to be regarded as 4 : 6-diphenyl-2-methylpyrylium compounds. Although the arguments of Schneider and Ross do not appear to be necessarily convincing, the author is led to share their view, since it is found that the action of benzaldehyde on the diphenylmethylpyrylium compounds gives 4 : 6-diphenyl-2-styrylpyrylium salts, the constitution of which is established by their production from styryl methyl ketone and phenyl styryl ketone.

H. W.

#### The Additive Product of Ammonia and 2-Methyl- $\beta$ -naphthachromone- $\alpha$ .

WILHELM SCHNEIDER and HELMUTH BODE (*Ber.*, 1923, 56, [B], 1042—1046).—In a previous communication (Schneider and Kunau, *A.*, 1921, i, 879), it has been mentioned incidentally that an additive product of ammonia and 2-methyl  $\beta$ -naphthachromone- $\alpha$  is formed in minor amount by the action of alcoholic ammonia on 3-acetyl-2-methyl- $\beta$ -naphthachromone- $\alpha$ . By a suitable modification of the experimental conditions, the substance may be made the main product of the change; it is remarkable, however, that it does not appear to be formed directly from

3-methyl- $\beta$ -naphthachromone- $\alpha$  and ammonia. It crystallises in slender, yellow needles, m. p. 138—139°, is soluble in alkalis and not too dilute acids, and gives an intense, dark green coloration with ferric chloride in alcoholic or ethereal solution. It gives a picrate,  $C_{20}H_{16}O_6N_4$ , yellow crystals, m. p. 179—180°. Its phenolic character is established by the isolation of a methyl ether, almost colourless crystals, m. p. 198° (corresponding picrate, yellow crystals, m. p. 171°). With benzoyl chloride and sodium hydroxide it loses the elements of water and gives a mono-benzoyl derivative, pale yellow crystals, m. p. 137°. The behaviour of the substance appears to be explained by the hypothesis



that it is 3-amino-2-methyl- $\beta$ -naphthachromone-4-ol (annexed formula I), and that the benzoyl derivative is an oxazole compound (formula II). H. W.

**Etheseroline.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, 176, 1480—1483; cf. A., 1918, i, 504).—The preparation of etheseroline has been further studied, all the intermediate substances have been isolated in a pure condition and the following new and corrected observations made. Eseretholemethine crystallises from ether in prismatic needles, m. p. 89°, and gives a picrate, m. p. 196°; two methiodides were obtained in admixture, their separation was effected by an ether-alcohol mixture. The  $\alpha$ -form is a crystalline powder of neutral reaction, m. p. 135°,  $\alpha_D + 2^\circ$ ; for the  $\beta$ -compound no m. p. is indicated, but  $\alpha_D - 25^\circ$ . The former is decomposed quantitatively into trimethylamine and etheseroline on being heated with concentrated sodium hydroxide solution, the latter is unaffected. Etheseroline,  $C_{14}H_{17}ON, H_2O$ , forms large, colourless, transparent prisms, m. p. 48°,  $\alpha_D$  (in 95% alcohol)  $-98^\circ$ ; it is a weak base, soluble in concentrated acids, but precipitated by addition of water. The nitrogen atom appears to be tertiary and to form part of a pyrrole or indole nucleus. It is linked to a methyl group. The substance has the double bond characteristic of eserine derivatives and also their asymmetric carbon atom.

H. J. E.

**The Pepper Taste of Piperine.** HEINRICH RHEINBOLDT (*Ber.*, 1923, 56, [B], 1228—1229).—The sharp taste of Indian pepper has been attributed alternately to the presence of piperine and chavicine. Piperine which has been exhaustively purified through its additive compound with tin tetrabromide has only a faint although distinct taste of pepper in substance, whereas in the finely disperse state or in alcoholic solution the physiological action is very marked. Piperine is therefore to be regarded as the active component of pepper (cf. Staudinger and Schneider, this vol., i, 361).

H. W.

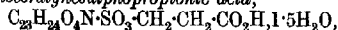
**Hydrolysis of Scopolamine.** RICHARD WILLSTÄTTER and ANDRÉ BERNER (*Ber.*, 1923, 56, [B], 1079—1082).—The basic constituent of scopolamine has not previously been isolated, since it is very readily transformed into scopoline (cf. Gadamer and Jammer, A., 1921, i, 588; Hees and Wahl, A., 1922, i, 854). It may, however, be obtained by the hydrolysis of scopolamine in weakly alkaline solution. This can be effected by pancreatic lipase in the presence of an ammonia-ammonium chloride buffer, activation being effected by the addition of albumin and calcium chloride; the presence of olive oil is advantageous. It is simpler, however, to use the mixture of ammonia and ammonium chloride alone; hydrolysis is almost complete after thirty-five days, but during this period a portion of the new base (for which the name "scopine" is proposed) is converted into scopoline, from which it can be separated only with difficulty. It is more advantageous, therefore, to limit the duration of the experiment, since scopoline is readily separated from unchanged scopolamine.

*Scopine* (annexed formula) crystallises in long, stable needles, m. p. 76° (corr.); it is optically inactive. It is converted when heated or under the influence of acid or, particularly, of alkalis into scopoline. *Scopine hydrochloride* crystallises from alcohol in well-defined platelets; the *picrate*, thin leaflets, has m. p. 231° (decomp.), whereas scopoline *picrate* forms coarser prisms, m. p. 236°. The two bases are, however, more readily distinguished in the chloroplatinates and chloroaurates. *Scopine chloroplatinate*,  $C_{23}H_{29}O_4N_2$ ,  $H_2PtCl_6 \cdot 2H_2O$ , crystallises in long, domatic prisms, n. p. 219° (decomp.), whereas scopoline chloroplatinate,  $+1H_2O$ , forms plates, m. p. 203° (decomp.). *Scopine chloroaurate*,  $\frac{1}{3}H_4O_2NAuCl_4$ , small prisms, m. p. 216° (decomp.), appears to contain water of crystallisation, whilst *scopoline chloroaurate*,  $+\frac{1}{2}H_2O$ , crystallises in prismatic plates, m. p. 220° (decomp.).

H. W.

#### Propionylpapaverine and Homocoralyne. WILHELM

SCHNEIDER and ERHARD NITZE (*Ber.*, 1923, 56, [B], 1036—1041).—In extension of previous work (Schneider and Schroeter, A., 1920, 760). *Homocoralyne sulphopropionic acid*,



yellow needles, m. p. 273° (decomp.) after previous softening, is readily obtained by treating papaverine with a mixture of propionic anhydride and sulphuric acid monohydrate which has previously been warmed at 85° until a test sample does not give a precipitate with barium chloride. The following derivatives are readily prepared from it: *chloride*,  $C_{23}H_{24}O_4NCl \cdot 3H_2O$ , slender, yellow needles, m. p. 250° (decomp.); *iodide*,  $+H_2O$ , slender, yellow needles, n. p. 268° (decomp.); *nitrate*,  $+2H_2O$ , yellow needles, which often and darken above 273° without melting; *hydrogen sulphate*,  $+2.5H_2O$ , gradual decomp. above 300°; *perchlorate*, slender, yellow needles, decomp. above 280°; *picrate*,  $+2H_2O$ , pale yellow, slender

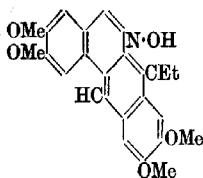
needles, m. p. 259° (decomp.). Treatment with sodium hydroxide solution causes the conversion of the sulphopropionic acid into *propionylpapaverine* (annexed formula), pale yellow, lustrous crystals m. p. 145—146° (the intermediate, quaternary ammonium base is very unstable). It gives a *phenylhydrazone*, colourless, lustrous needles, m. p. 205—206°; an *oxime*, small, almost colourless needles, m. p. 212°, and a *methiodide*, yellow crystals, m. p. 215—216° (prepared by treating the ketonic base with methyl iodide and benzene at 100°). The substance last mentioned is converted by sodium hydroxide solution into *N-methylpropionylisopapaverine*,  $C_{24}H_{27}O_5N$ , a yellow, amorphous powder, m. p. 120—121°.

Homocoralyne, in the form of its sulphopropionate, is reduced by zinc filings and dilute sulphuric acid in the presence of acetic acid to an intensely yellow, unstable base which appears to be dihydrohomocoralyne. More drastic reduction converts it into *hexahydrohomocoralyne* [*homocoralydine*],  $C_{23}H_{29}O_4N$ , large, colourless leaflets, m. p. 145—146° (*hydriodide*; slender, colourless leaflets, m. p. 236°).  
H. W.

**Strychnine.** I. E. OLIVERI-MANDALÀ and G. COMELLA (*Gazzetta*, 1923, 53, i, 276—284).—According to the structure proposed by Perkin and Robinson (T., 1910, 97, 305), strychnine contains a secondary alcohol grouping, which forms part of a hydrogenated aromatic nucleus. The action of a halogen, bromine especially, in presence of water should, therefore, convert strychnine into a cyclohexanone derivative which, by further oxidation and consequent rupture of the hydroaromatic nucleus, should give rise to a dicarboxylic acid, or by a series of transformations should be capable of conversion into a dehydrogenated ring containing the hydroxyphenyl grouping.

The only product obtained by the authors by treating the free base with bromine water in presence of calcium carbonate is, however, monobromostrychnine (cf. Beckurts, A., 1885, 675, 911; Leuchs and Boll, A., 1910, i, 766). Treatment of strychnine oxide (cf. Pictet and Mattisson, A., 1905, i, 816) with bromine or potassium ferricyanide also fails to oxidise any functional group of the strychnine molecule, and the action of hydrogen peroxide on strychnine in acetic acid solution gives a similar result.

From various considerations, the conclusion is drawn that the cause of the isomerism of strychnine and *isostrychnine* lies in the carbon atom united with the oxygen atom, the function of which is not fully understood. None of the reagents for characterising oxygen atoms in different groupings seems capable of determining the form in which this oxygen atom exists, but the presence of the group  $\cdot N \cdot CMe(OH) \cdot$  is in agreement with the behaviour of strychnine, and the conversion of such group into  $\cdot NH \cdot + \cdot CO \cdot CH_3 \cdot$  would explain the appearance of the ketonic function attending the transformation of strychnine into *isostrychnine*.



Oxidation of strychnine oxide by permanganate in the cold yields the acid,  $C_{21}H_{20}O_6N_2 \cdot 2H_2O$ , obtained by Leuchs (A., 1908, 563) by the oxidation of strychnine, suspended in acetone, by means of permanganate. Oxidation of the oxide by hot permanganate gives, however, a compound, m. p. about  $200^\circ$  (decomp.), which is undoubtedly a derivative of indole, the presence of an indole nucleus in the strychnine molecule being, therefore, certain.

T. H. P.

**Some Transformations of 2:4-Dimethylpyrrole.** HANS FISCHER, BERNHARD WEISS, and MAX SCHUBERT (*Ber.*, 1923, 56, B), 1194—1202).—Further experiments with 2:4-dimethylpyrrole are recorded (cf. Fischer and Bäumer, A., 1915, i, 309; Fischer and Zerweck, A., 1922, i, 758; this vol., i, 364).

2:4-Dimethylpyrrole condenses with acetonitrile in anhydrous ether under the influence of hydrogen chloride to give the *ketimine* of 5-acetyl-2:4-dimethylpyrrole, slender needles, m. p.  $141^\circ$ , in which the new side chain is only loosely attached, since it is removed by the action of hydrogen in the presence of spongy platinum with re-formation of 2:4-dimethylpyrrole. The ketimine is converted by boiling water into 5-acetyl-2:4-dimethylpyrrole, colourless needles, m. p.  $121^\circ$ , which is conveniently prepared in this manner. It does not appear capable of further condensation.

5-Chloroacetyl-2:4-dimethylpyrrole, 
$$NH \begin{array}{c} \diagup C(CO \cdot CH_2Cl) \cdot CMe \\ \diagdown CMe = CH \end{array}$$

colourless needles, m. p.  $143^\circ$ , is prepared from 2:4-dimethylpyrrole and chloroacetonitrile; the intermediate production of a stable ketimine is not observed. It is converted by dimethylamine in absolute alcoholic solution into 5-dimethylaminoacetyl-2:4-dimethylpyrrole, m. p.  $110^\circ$ . 5-Chloroacetyl-2:4-dimethylpyrrole and formaldehyde yield *bis*-5-chloroacetyl-2:4-dimethylpyrrolmethane, 
$$H_2C \cdot CO \cdot C \cdot CMe \begin{array}{c} \gg C \cdot CH_2 \cdot C \leq CMe \cdot C \cdot CO \cdot CH_2Cl \\ HN \cdot CMe \quad CMe \cdot NH \end{array}$$
, m. p.  $258^\circ$ , from

which *bis*-5-dimethylaminoacetyl-2:4-dimethylpyrrolmethane, colourless needles, m. p.  $170^\circ$  after previous softening, is obtained in the usual manner.

2:4-Dimethylpyrrole is converted by formic acid (90%) in the presence of perchloric acid into *bis*-2:4-dimethylpyrrolmethane perchlorate,  $C_{12}H_{12}O_4N_4Cl$ , reddish-brown needles which become discoloured at  $200^\circ$ , but do not melt below  $260^\circ$ ; the corresponding

base, 
$$\begin{array}{c} CH \cdot CMe \\ CMe \cdot NH \end{array} \gg C \cdot CH \cdot C \begin{array}{c} \leq CMe \cdot CH \\ N = CMe \end{array}$$
, crystallises in yellow needles,

m. p.  $117^\circ$ .

Ethyl 2:4-dimethylpyrrole-5-carboxylate, m. p.  $125^\circ$ , is prepared by the successive addition of ethereal solutions of 2:4-dimethylpyrrole and ethyl chloroformate to magnesium ethyl bromide dissolved in ether; it is hydrolysed by potassium hydroxide solution (50%) to 2:4-dimethylpyrrole-5-carboxylic acid, m. p.  $136^\circ$ , which is also obtained directly by the action of carbon dioxide on the Grignard compound from 2:4-dimethylpyrrole. The ester is converted by the hydrocyanic acid method into 5-carbethoxy-

2:4-dimethylpyrrole-3-aldehyde,  $\text{NH} \begin{array}{c} \text{C}(\text{CO}_2\text{Et})\text{CMe} \\ \text{CMe}=\text{C}\cdot\text{CHO} \end{array}$ , needles,

m. p. 145°, which is hydrolysed to the corresponding acid, m. p. 230° after previous partial decomposition. The latter compound is transformed by dry distillation into 2:4-dimethylpyrrole-3-aldehyde, m. p. 126°, in which a second aldehyde group could not be introduced by means of hydrocyanic acid. 5-Carboethoxy-2:4-dimethylpyrrole-3-aldehyde gives a phenylhydrazone, m. p. 204°, an azlactone,  $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$ , m. p. 232°, an oxime, m. p. 196—197° (which is converted into ethyl 3-cyano-2:4-dimethylpyrrole-5-carboxylate, m. p. 171°, by anhydrous sodium acetate and acetic anhydride), and a semicarbazone, m. p. 285° (decomp.). The latter substance is converted by alcoholic sodium ethoxide solution at 160—170° into 2:3:4-trimethylpyrrole which is identified as the picrate.

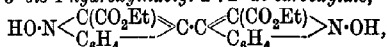
Ethyl 2:4-dimethylpyrrole-5-carboxylate is converted by chloroacetonitrile into ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 163°, which is transformed by potassium cyanide into ethyl 3-cyanoacetyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 172—173°.

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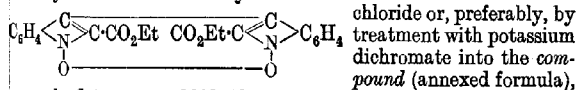
**Ethyl o-Nitrobenzylacetoacetate and its Transformations.** S. GABRIEL, WILH. GEEHARD, and R. WOLTER (*Ber.*, 1923, 56, [2], 1024—1036).—Ethyl o-nitrobenzylacetoacetate, a pale, brownish-yellow liquid, b. p. about 180°/1 mm., is prepared by the addition of a solution of a molecular proportion of o-nitrobenzyl chloride in alcohol to a similar solution of two molecular proportions of ethyl acetoacetate and two atomic proportions of sodium and subsequent preservation of the mixture for two days. It is readily converted by alcoholic potassium hydroxide solution into a mixture of ethyl 1-hydroxyindole-2-carboxylate,  $\text{C}_8\text{H}_4 \begin{array}{c} \text{CH} \\ \text{N}(\text{OH}) \end{array} \text{C}\cdot\text{CO}_2\text{Et}$ , coarse needles, m. p. 64—65°, and 1-hydroxyindole-2-carboxylic acid, m. p. 159·5° (the potassium salt,  $\text{C}_{11}\text{H}_{10}\text{O}_3\text{NK}$ , lemon-yellow leaflets, and the unstable ammonium salt, lemon-yellow needles, of the ester are described). The ethyl ester is converted by sodium methoxide and methyl iodide at 100° into methyl 1-methoxyindole-2-carboxylate, needles, m. p. 63—64°, and by ethylation into ethyl 1-ethoxyindole-2-carboxylate, from which 1-ethoxyindole-2-carboxylic acid, colourless needles, m. p. 150—151°, is prepared. 1-Benzoyloxyindole-2-carboxylic acid has m. p. 168—169° (decomp.); it gives a methyl ester, pointed, flattened needles, m. p. 82—83°, and an ethyl ester, m. p. 77—78°. Ethyl 1-benzoyloxyindole-2-carboxylate forms crystals, m. p. 104—105°, whilst ethyl 1-acetoxyindole-2-carboxylate crystallises in needles, m. p. 76—77°. Chlorination of the ester in the presence of carbon tetrachloride yields a di-chloro-ester,  $\text{C}_{11}\text{H}_5\text{O}_3\text{NCl}_2$ , m. p. 98—99°. A tribromo-compound,  $\text{C}_{11}\text{H}_3\text{O}_3\text{NBBr}_3$ , small needles, m. p. 138·5°, is obtained from the ester and bromine in the presence of glacial acetic acid, whereas a monobromo-derivative, rhombohedra, m. p. 82—84°, is formed when benzene is used as solvent. Ethyl 1-hydroxyindole-2-carboxylate is reduced by hydriodic acid and phosphonium iodide, or, more conveniently,

by stannous chloride in the presence of glacial acetic and fuming hydrochloric acids to *ethyl indole-2-carboxylate*, m. p. 125–126°, which is converted in the usual manner into *indole-2-carboxylic acid*, m. p. 203°; the latter substance is transformed by thionyl chloride into a mixture of the corresponding chloride and anhydride. *Ethyl indole-2-carboxylate* is converted by bromotrimethane into *ethyl 3-bromoindole-2-carboxylate*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CBr} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$ , pale yellow needles, m. p. 152–153°, which is hydrolysed by potassium hydroxide solution to *3-bromoindole-2-carboxylic acid*, slender needles, m. p. 199° (decomp.). *Ethyl 3-chloroindole-2-carboxylate*, needles, m. p. 153–154°, is obtained when an intimate mixture of *ethyl indole-2-carboxylate* and phosphorus pentachloride is heated on the steam-bath, whereas, at a higher temperature, a *bichloro-derivative*,  $\text{C}_{11}\text{H}_8\text{O}_2\text{NCl}_2$ , needles, m. p. 194–195°, is produced. *3-Chloroindole-2-carboxylic acid*, m. p. 180–182° (decomp.), is transformed by thionyl chloride into the corresponding *chloride*, a greyish-yellow, crystalline mass; it is readily reduced by hydriodic acid and phosphonium iodide to *indole-2-carboxylic acid*.

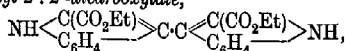
*Ethyl 1-hydroxyindole-2-carboxylate* is oxidised by cautious treatment with ferric chloride in the presence of acetic acid (50%) to *ethyl 3:3'-bis-1-hydroxyindolyl-2:2'-di-carboxylate*,



pale yellow, crystalline needles, m. p. 152–153° (decomp.); the corresponding *potassium salt*, the *dimethyl ether*, a colourless, crystalline powder, m. p. 129° after softening at 126°, and *3:3'-bis-1-hydroxyindolyl-2:2'-dicarboxylic acid*, microscopic rhombs, gradual decomp. 250–270°, are described. *Ethyl 1-hydroxyindole-2-carboxylate* is converted by more drastic oxidation with ferric



green leaflets, m. p. 189° (decomp.), which is reduced by stannous chloride in the presence of acetic and hydrochloric acids to *ethyl 3:3'-bis-indolyl-2:2'-dicarboxylate*,



colourless needles, m. p. 225–226°; the latter ester is also obtained by the reduction of *ethyl 3:3'-bis-1-hydroxyindolyl-2:2'-dicarboxylate*, preferably by means of stannous chloride. It is hydrolysed by potassium hydroxide solution to *3:3'-bis-indolyl-2:2'-dicarboxylic acid*,  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$ , a crystalline powder, m. p. above 285°, the *potassium salt* and *ammonium salt*, rhombic leaflets, of which are described. Thionyl chloride transforms the acid into the corresponding *chloride*, a lemon-yellow, crystalline powder which becomes red at 170–180°, but does not melt below 290°, from which the *ethyl ester*, m. p. 225–226°, and the *methyl ester*, pale yellow prisms or plates, m. p. 318–320°, are prepared. The acid loses carbon

dioxide and water when heated in a vacuum at above  $280^{\circ}$ , and yields  $\alpha$ -bis-3 : 3'-indolyl,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{NH}$ , colourless rhombs, m. p. about  $286$ — $287^{\circ}$ , in a sealed capillary, which is converted by hydriodic or hydrobromic acid in the presence of glacial acetic acid into the salt of the isomeric  $\beta$ -base (see later).

Ethyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate is converted by hydriodic and glacial acetic acids under the conditions customary in estimation of alkoxy-groups into ethyl 3 : 3'-bis-indolyl-2 :

carboxylate,  $\text{NH} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}(\text{CO}_2\text{Et}) \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NH}$ , short, pale-yellow

prisms or plates, m. p.  $172$ — $173^{\circ}$ , which gives a yellow iodide,  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_2\text{HI}$ , flattened needles, and a brown *per*-iodide,  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_2\text{HI}_2$ , which inhibit complete de-alkylation owing to their sparing solubility in the Zeisel mixture. The ester is hydrolysed to 3 : 3'-bis-indolyl-2-carboxylic acid, chrome-red needles, m. p.  $209$ — $210^{\circ}$ . Treatment of ethyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate with colourless hydriodic and glacial acetic acids in the presence of phosphonium iodide yields  $\beta$ -bis-3 : 3'-indolyl, m. p.  $207$ — $208^{\circ}$ ; the corresponding *hydrobromide*,  $\text{C}_{19}\text{H}_{16}\text{N}_2\text{HBr}$ , lemon-yellow needles, and *hydriodide*, are described.

Methyl 1-hydroxyindole-2-carboxylate, m. p.  $100$ — $101^{\circ}$ , is oxidised in a similar manner by ferric chloride to methyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate,  $(\text{C}_{10}\text{H}_8\text{O}_2\text{N})_2$ , yellow needles, m. p.  $209$ — $210^{\circ}$  (decomp.) after softening at  $160^{\circ}$ , and by potassium dichromate to the compound,  $(\text{C}_{10}\text{H}_7\text{O}_2\text{N})_2$ , reddish-brown crystals which appear green by reflected light. Methyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate is reduced by stannous chloride to methyl 3 : 3'-bisindolyl-2 : 2'-dicarboxylate, m. p.  $318$ — $320^{\circ}$ .

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**2 : 8-Diamino-5-benzyl-10-methyldihydroacridine.** P. KARRER (*Helv. Chim. Acta*, 1923, **6**, 409—411).—This compound is obtained by the action of benzyl-magnesium bromide on the hydrochloride of 2 : 8-diamino-10-methylacridinium chloride. 2 : 8-Diamino-5-benzyl-10-methyldihydroacridine forms white, felted needles, it is unusually stable, and only becomes yellow very slowly in air. The *dihydrochloride* forms colourless needles which rapidly redden in air.

E. H. R.

**The Use of Rhodanine in Organic Syntheses. II. Amino acids and Ketonic Acids.** CH. GRÄNACHER, M. GERÖ, A. OFNER, A. KLOPFENSTEIN, and E. SCHLATTER (*Helv. Chim. Acta*, 1923, **6**, 458—467).—Continuing previous work (A., 1922, i, 849), a number of new condensation products of rhodanine with aldehydes have been prepared and their decomposition products studied. The condensation products crystallise with unusual facility, but the  $\alpha$ -thiolcarboxylic acids obtained by their alkaline decomposition are difficult to crystallise in the aromatic series, and in the aliphatic series are generally oily substances which cannot be distilled without decomposition.

5-Ethylidenerhodanine,  $\begin{matrix} \text{NH-CO} \\ \text{CS-S} \end{matrix} > \text{C:CHMe}$ , obtained by condensing

rhodanine with paracetaldehyde in boiling acetic acid, forms lustrous, brownish-yellow leaflets, m. p. 143°. 5-Crotonylidenerhodanine, from rhodanine and crotonaldehyde, crystallises in brownish-yellow needles, m. p. 189°. 5-isoValerylidenerhodanine forms brownish-yellow leaflets, m. p. 83°. 5-Phenylethylidenerhodanine, from phenylacetaldehyde and rhodanine, forms lustrous, yellow needles, m. p. 217°. Rhodanylidene-glyoxylic [rhodanylidene-glyoxylic] acid,  $\begin{matrix} \text{NH-CO} \\ \text{CS-S} \end{matrix} > \text{C:CH-CO}_2\text{H}$ , obtained by condensing glyoxylic

acid with rhodanine, crystallises in lustrous, brownish-red scales, decomposing without melting at 225°; its ethyl ester is a yellow, crystalline powder, and its potassium salt, which crystallises with one mol. of potassium hydroxide, is a brownish-yellow, crystalline powder.

$\alpha$ -Thiol-p-methoxycinnamic acid, obtained by heating anisylidenerhodanine with 15% sodium hydroxide solution, forms golden-yellow crystals, m. p. 178°; the yield is nearly theoretical. With hydroxylamine in boiling alcohol it gives  $\alpha$ -oximino-p-anisylpropionic acid, white needles, m. p. 159°, from which p-anisylpyruvic acid can be obtained. When reduced with sodium amalgam, the oxime gives p-anisylalanine.  $\alpha$ -Thiolmethylenedioxy-cinnamic acid, obtained by the action of alkali on piperonylidenerhodanine; with hydroxylamine it gives  $\alpha$ -oximinomethylenedioxyphenylpropionic acid, lustrous, yellow leaflets, m. p. 156–158°, which is reduced by sodium amalgam and alcoholic lactic acid to methylenedioxyphenylalanine, white leaflets, m. p. 250–255°.  $\alpha$ -Thiol-p-isopropylcinnamic acid is obtained from cuminyldenerhodanine; it is a yellow, amorphous powder, which with hydroxylamine gives  $\alpha$ -oximino-p-isopropylphenylpropionic acid, white, felted needles, m. p. 170°. Hydrolysis of the oxime gives p-isopropylphenylpyruvic acid, needles or leaflets, m. p. 140–150°, and reduction of the oxime gives p-isopropylphenylalanine, granular aggregates melting at 230°, m. p. 255°. E. H. R.

The Preparation and Properties of 4':4''-Tetramethylaminoanthrafuchsone. FREDERICK ALFRED MASON (T., 1923, 23, 1548–1559).

Synthetic Experiments with the Fission Products of the Blood Pigments and the Formation of Complex Salts from Pyrrylmethenes. I. HANS FISCHER and MAX SCHUBERT (Ber., 1923, 56, [B], 1202–1211).—It has been shown previously that the blood pigments contain compounds in which the pyrrole nuclei are united by carbon atoms in the  $\alpha$ -position. The synthetic methods used hitherto in the preparation of similar substances are inadequate, since they only allow the union of two similar nuclei and it has been shown, for example, in the case of bilirubin, that the compound is formed from a basic hydroxypyrrole and a pyrrolecarboxylic acid. The synthesis of pyrrolealdehydes

has therefore been attempted with the ultimate object of condensing them with a second selected pyrrole component. The experiments now described are chiefly effected with cryptopyrrole (2 : 4-dimethyl-3-ethylpyrrole).

The formation of complex compounds containing copper and the dipyrromethene group has been investigated. Although the spectroscopic behaviour of these compounds is not completely analogous to that of the blood pigments, the authors consider that their results prove that the structure of the dipyrromethenes is closely related to that of the latter compounds.

Attempts to secure a better method for the preparation of cryptopyrrole are described. The *semicarbazone* of 3-acetyl-2 : 4-dimethylpyrrole, m. p. 203—204°, is crystalline and reducible by sodium ethoxide, but the yields are so poor that the method has no practical significance. In confirmation of previous experiments, the corresponding hydrazone could not be isolated by reason of its very pronounced tendency to give the ketazine. On the other hand, ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate readily yields the corresponding hydrazone,  $\text{NH} \begin{array}{c} \diagup \text{C}(\text{CO}_2\text{Et})\cdot\text{CMe} \\ \diagdown \text{CMe} \end{array} = \text{C} \cdot \text{CMe} \cdot \text{N} \cdot \text{NH}_2$ , m. p.

137°, which is converted (without being isolated) by sodium ethoxide solution into 2 : 4-dimethyl-3-ethylpyrrole (picrate, m. p. 136°), the yield being in some cases 50% of that theoretically possible. Cryptopyrrole is transformed by chloroacetonitrile into 5-chloroacetyl-2 : 4-dimethyl-3-ethylpyrrole, colourless needles, m. p. 140°, from which 5-dimethylaminoacetyl-2 : 4-dimethyl-3-ethylpyrrole hydrochloride, colourless needles, m. p. 201—202°, is derived.

Cryptopyrrole dissolved in chloroform is converted by anhydrous hydrocyanic acid and hydrogen chloride into C-dicryptopyrromethylamine, m. p. 142°, which is transformed by boiling water into 2 : 4-dimethyl-3-ethylpyrrole-5-aldehyde, colourless needles, m. p. 105—106°; the corresponding oxime, colourless needles, m. p. 118°, and its picrate, m. p. 155°; the *semicarbazone*, colourless needles, m. p. 203°, and its picrate, m. p. 162°, are described. The *semicarbazone* is reduced by sodium ethoxide solution at 150—160° to phyllopyrrole, which is identified as the picrate, m. p. 104°.

2 : 4-Dimethyl-3-ethylpyrrole-5-aldehyde condenses with ethyl 2 : 4-dimethylpyrrole-3-carboxylate in the presence of concentrated hydrochloric acid to give bis-3-carbethoxy-2 : 4-dimethylpyrromethene,  $\text{CO}_2\text{Et} \cdot \text{C} \cdot \text{CMe} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{C} \begin{array}{c} \diagup \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \diagdown \text{N} = \text{CMe} \end{array} \\ \diagdown \text{MeC} \cdot \text{NH} \end{array}$ , m. p. 189°; the carbon bridge is derived from the pyrrolealdehyde, which loses its aldehydic group as formic acid. The course of the reaction is somewhat unexpected, since the aldehydic group is relatively firmly attached. Bis-2 : 4-dimethyl-3-ethylpyrromethene perchlorate  $\begin{array}{c} \text{CEt} \cdot \text{CMe} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{C} \begin{array}{c} \diagup \text{CMe} = \text{CEt} \\ \diagdown \text{N}(\text{HClO}_4) \cdot \text{CMe} \end{array} \\ \diagdown \text{MeC} \cdot \text{NH} \end{array} \end{array}$ , coarse, red needles, decompose at 240° after becoming discoloured at 170°, is obtained by the condensation of 2 : 4-dimethyl-3-ethylpyrrole-5-aldehyde in alcohol solution in the presence of perchloric acid. Molar quantities of

cryptopyrrolealdehyde and cryptopyrrolecarboxylic acid in the presence of concentrated hydrochloric acid give 2:4-dimethyl-3-ethylpyrrolmethenyl-2:4-dimethylpyrrol-3-propionic acid, hydrochloride,  $\begin{array}{c} \text{CMe} \cdot \text{CMe} \\ | \quad | \\ \text{C} \cdot \text{CH} : \text{C} \\ | \quad | \\ \text{CMe} \cdot \text{NH} \end{array} > \begin{array}{c} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \\ \text{N(HCl)} \cdot \text{CMe} \end{array}$ , brownish-red needles, m. p. 215°, whilst the aldehyde and hæmopyrrolecarboxylic acid yields 2:4-dimethyl-3-ethylpyrrolmethenyl-2:3-dimethylpyrrol-4-propionic acid hydrochloride,  $\begin{array}{c} \text{CMe} \cdot \text{CMe} \\ | \quad | \\ \text{C} \cdot \text{CH} : \text{C} \\ | \quad | \\ \text{CMe} \cdot \text{NH} \end{array} > \begin{array}{c} \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CMe} \\ | \\ \text{N(HCl)} \end{array}$ , brownish-red needles, m. p. 220°.

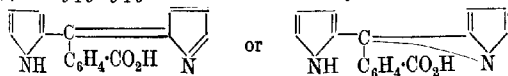
The copper salt of bis-2:4-dimethylpyrrolmethene (annexed formula) is precipitated in green needles when a solution of the methene in alcohol is treated with an ammoniacal copper solution. Copper salts are prepared in a similar manner from 2:4-dimethyl-3-ethylpyrrolmethenyl-2:4-dimethylpyrrol-3-propionic acid (reddish-brown needles), 2:4-dimethyl-3-ethylpyrrolmethenyl-2:3-dimethylpyrrol-4-propionic acid and from bis-hæmopyrrolecarboxylic estermethene.

3-Acetyl-2:4-dimethylpyrrole-5-carboxylamide, m. p. 260°, is obtained by the action of concentrated aqueous ammonia on the corresponding ethyl ester at 150–160°. H. W.

**Pyrrole Group. XIV. Syntheses by Means of Magnesium-Pyrrol Halides. Pyrrolephthalein.** BERNARDO ODDO and FRANCESCO TOGNACCHINI (*Gazzetta*, 1923, 53, i, 265–270).—The action of magnesium pyrrol bromide on phthalyl chloride in ethereal solution yields the following two compounds.

(1) *Pyrrolephthalein*,  $\text{CO} < \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{O} \end{array} > \text{C} \begin{pmatrix} \text{NH} \cdot \text{CH} \\ | \\ \text{CH} \cdot \text{CH} \end{pmatrix}_2$ , which forms white, lozenge-shaped crystals, m. p. 202°, and with silver nitrate solution and a drop of aqueous ammonia gives a white precipitate which immediately redissolves. When heated in acid solution, it undergoes resinification, with formation of phenylpyrrolpyrrolene-nethane-o-carboxylic acid, pyrrolene-phthalide, and pyrrole. In freezing acetic acid, it has the normal molecular weight.

(2) *Phenylpyrrolpyrrolene-methane-o-carboxylic acid*,



which is formed also when pyrrolephthalein is boiled with 20% sodium hydroxide solution, crystallises in almost white, silky needles, m. p. about 130°. After some time, it undergoes transformation into a compound, m. p. about 153°, owing probably to elimination of a molecule of water from the carboxyl and imino-

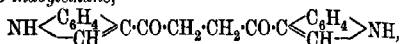
groups; if this product is recrystallised from water, the melting point resumes its original value.

When either of these compounds is coupled in alkaline solution with diazobenzene chloride, it yields a *compound*, which forms silky, reddish-brown crystals, m. p. 126°, and is probably benzene-bisazopyrrolephthalein. Treatment of a trace of this compound with concentrated sulphuric acid yields an ultramarine coloration changing to reddish-purple on dilution; concentrated nitric acid gives a deep violet solution, which yields a red precipitate on dilution, and concentrated hydrochloric acid gives a violet coloration, turning in a few seconds to yellow. Towards alkali, it behaves similarly to pyrrolephthalein.

T. H. P.

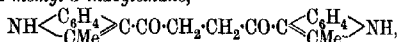
**Synthesis of  $\gamma$ -Diketones in the Indole Group.** G. SANNA (*Gazzetta*, 1923, 53, i, 177—182; cf. this vol., i, 57, 59).—In its action on magnesium derivatives of indole and 2-methylindole, succinyl chloride behaves in accordance with its symmetrical formula, the products being diketonic and not lactonic in character.

$\alpha\beta$ -Di-3-indoylethane,

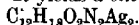


prepared by the action of succinyl chloride on magnesium indolyl bromide, forms minute, colourless prisms, m. p. 287°, exhibits normal cryoscopic behaviour in acetic acid, and dissolves in sulphuric acid, giving a yellow and then a rust-red coloration changing to green on heating. It forms a dirty white, pulverulent *silver* derivative,  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_2\text{Ag}_2$ , and, when heated in a sealed tube at 140—150° with alcoholic ammonia solution, yields a small proportion of a yellow compound, m. p. 254°, which is possibly di-indylpyrrole,  $\text{C}_{20}\text{H}_{12}\text{N}_2$ . It yields a *dioxime*,  $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_4$ , which forms blade-like, colourless, prismatic crystals, m. p. 305° (decomp.).

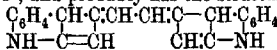
$\alpha\beta$ -Di-2-methyl-3-indoylethane,



obtained similarly from magnesium 2-methylindolyl bromide, crystallises in minute prisms, m. p. 297° (decomp.), has the normal molecular weight in freezing acetic acid, and dissolves in sulphuric acid, giving a blood-red solution, which becomes violet and then purple-red when heated. It yields a *silver* derivative,



When heated in a closed tube with alcoholic ammonia solution it yields: (1) a small proportion of a yellow, microcrystalline powder, m. p. 237°, which is probably dimethylketopyrrole,  $\text{C}_{22}\text{H}_{18}\text{N}_2$ ; (2) a *compound*,  $\text{C}_{22}\text{H}_{18}\text{N}_2$ , which crystallises in tabular prisms, m. p. 285°, and probably has the structure

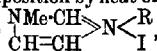


(cf. this vol., i, 59). The *dioxime* of  $\alpha\beta$ -di-2-methyl-3-indoylethane,  $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_4$ , crystallises in prisms, m. p. 267°.

T. H. P.

**Quaternary Salts of Glyoxalines.** JEAN SARASIN (*Hd. Chim. Acta*, 1923, 6, 370—376).—It has been shown by Pym

(T., 1910, 97, 1815) that 1:4- and 1:5-dimethylglyoxalines give the same methiodide, showing that the halogen is mobile between the two nitrogen atoms. The author has investigated the effect of this kind of tautomerism on the decomposition by heat of quaternary salts of 1-methylglyoxaline of the type



in which the radicle R has been varied. The methiodide when heated in a vacuum decomposes completely into methyl iodide and 1-methylglyoxaline. The ethiodide gives a mixture of methyl and ethyl iodides and of 1-methyl- and 1-ethyl-glyoxalines, and the isoamyliodide behaves in a similar manner. On the other hand, 1-methylglyoxaline benzylbromide gives no trace of 1-benzylglyoxaline when heated.

When the quaternary salts of Wallach's 4(or 5)-chloro-1-methylglyoxaline are heated, they give rise to a new series of 5(or 4)-chloro-1-alkylglyoxalines, having higher boiling points than their isomerides. It can be supposed that, owing to repulsion between chlorine and iodine, the methiodide of 4(5)-chloro-1-methylglyoxaline will have the formula



it will lose the methyl group attached to the 1-nitrogen atom. The new product must therefore be 5-chloro-1-methylglyoxaline, and Wallach's compound can only be 4-chloro-1-methylglyoxaline.

The quaternary salts of 4-chloro-1-methylglyoxaline are stable and well crystallised; the *methiodide* has m. p. 174—175°, *ethiodide*, m. p. 156—157°, *isoamyliodide*, m. p. 118—119°, *allylbromide*, m. p. 141—142°, *benzylbromide*, m. p. 107—109°. 5-Chloro-1-methylglyoxaline is a liquid, b. p. 250—252°; its *picrate* has m. p. 166—167°. 5-Chloro-1-ethylglyoxaline, obtained by heating 4-chloro-1-methylglyoxaline ethiodide, has b. p. 258—260°; its *picrate* has m. p. 146—147°. 5-chloro-1-isoamyglyoxaline, obtained by heating the above *isoamyliodide*, has b. p. 286—288°; its *picrate* has no definite m. p. 5-Chloro-1-allylglyoxaline has b. p. 129—131°/12 mm. and decomposes when distilled at the ordinary pressure; *picrate*, m. p. 110—113°. The 5-chloro-1-alkylglyoxalines are reduced by sodium and alcohol to 1-alkylglyoxalines, but 1-allylglyoxaline cannot be obtained in this way. 4-Chloro-1-methylglyoxaline benzylbromide does not give 5-chloro-1-benzylglyoxaline when heated.

E. H. R.

**New Syntheses in the Glyoxaline Group.** JEAN SARASIN (*Helv. Chim. Acta*, 1923, 6, 377—385).—Attempts to obtain an allyl derivative of glyoxaline from 4-chloro-1-methylglyoxaline and allyl chloride by Fittig's reaction were unsuccessful. The 4-chlorine atom is very resistant and is not affected by a Grignard reagent, ethyl sodiomalonate, diethylamine, or potassium iodide at temperatures up to 150°. When heated with 40% formaldehyde in a sealed tube at 120°, 4-chloro-1-methylglyoxaline is transformed quantitatively into 4-chloro-1-methyl-2-hydroxymethylglyoxaline, a colourless, crystalline compound, m. p. 109—110°, forming a *picrate*, m. p. 148—150°. When reduced with hydriodic acid and red

phosphorus, this gives 1:2-dimethylglyoxaline. Chloral forms with 4-chloro-1-methylglyoxaline an unstable compound, m. p. 82—85°, b. p. 150°/15 mm.

The synthesis of 4(5)-methyl-5(4)-allylglyoxaline was effected as follows. Oximinallyacetone,  $\text{CH}_3\text{CO}\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_5$ , was reduced to aminallyacetone,  $\text{CH}_3\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{C}_6\text{H}_5$ , the hydrochloride of which has m. p. 152—153° (decomp.). When this is heated with ammonium thiocyanate in aqueous solution it forms, nearly quantitatively, 2-mercapto-4(5)-methyl-5(4)-allylglyoxaline, m. p. 238—239°, which when oxidised with ferric chloride is converted into 4(5)-methyl-5(4)-allylglyoxaline, m. p. 71—72°, b. p. 180—181°/12 mm.; yield 50%, but lower when other oxidising agents such as potassium persulphate or hydrogen peroxide are used. When this methylallyglyoxaline is methylated with methyl iodide it gives a mixture of 1:4-dimethyl-5-allyl- and 1:5-dimethyl-4-allyl-glyoxalines, which were not separated.

When heated with hydrobromic acid in acetic acid solution, 4(5)-methyl-5(4)-allylglyoxaline is converted into 4(5)-methyl-5(4)- $\beta$ -bromopropylglyoxaline, m. p. 109—110°, which is converted by ammonia into 4(5)-methyl-5(4)- $\beta$ -aminopropylglyoxaline, b. p. 185—186°/10 mm. The dihydrochloride, which is very hygroscopic, has m. p. 215—217°, and the dipicrate, 229—230°. With diethylamine, the above bromo-compound reacts to give 4(5)-methyl-5(4)-diethylaminopropylglyoxaline, b. p. 143—144°/2 mm.; dihydrochloride, m. p. 199—200°; dipicrate, m. p. 178—179°. When 4(5)-methyl-5(4)-allylglyoxaline is treated with bromine in carbon disulphide, 4(5)-methyl-5(4)- $\beta$ -dibromopropylglyoxaline, m. p. 116—117°, is formed, and with iodine chloride, 4(5)-methyl-5(4)- $\beta$ -chloriodopropylglyoxaline, m. p. 94—95° (decomp.). Attempts to eliminate a single atom of halogen from these dihalogen compounds with potassium hydroxide or sodium ethoxide were unsuccessful.

E. H. R.

**The Isomerism of Reduced Derivatives of Quinoxaline. I. The Four Stereoisomeric 2:3-Diphenyl-1:2:3:4-Tetrahydroquinoxalines.** GEORGE MACDONALD BENNETT and CHARLES STANLEY GIBSON (T., 1923, 123, 1570—1575).

**Barbituric Acid. II.** WALTER BOCK (Ber., 1923, 56, [B], 1222—1227; cf. this vol., i, 64).—A solution of barbituric acid in water is converted by the requisite quantity of gaseous chlorine into 5-chlorobarbituric acid, long needles, m. p. 290—295° after slight previous decomposition (ammonium salt, prismatic crystals, m. p. 245° [decomp.] after becoming discoloured at 200°), or 5:5-dichlorobarbituric acid, colourless crystals, decomp. 209—211°. 5-Chlorobarbituric acid may also be obtained by the action of aqueous hydrochloric acid on the 5-bromo-acid; it is relatively very stable towards boiling water. Attempts to prepare 5-bromobarbituric acid from the 5-chloro-acid and hydrobromic acid were unsuccessful, probably by reason of the limited stability of the bromo-acid in boiling aqueous solution.

5:5'-Dichlorohydurilic acid is readily hydrolysed by boiling

water to 5-chlorobarbituric acid and alloxan:  $C_4H_4O_6N_4Cl_2 + H_2O = C_4H_3O_5N_4Cl + C_4H_2O_4N_4 + HCl$ . Ammonium 5:5'-dichloro-*hydrurilate* forms colourless or pale pink, hydrated crystals ( $+2.5H_2O$ ), whereas the anhydrous compound is dark red; it has m. p. about  $235^\circ$  after becoming discoloured at  $140^\circ$ .

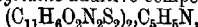
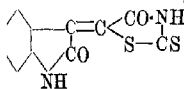
5:5-Dichlorobarbituric acid is transformed by the prolonged action of chlorine into trichloroacetylcarbamide; the course of the reaction appears to be somewhat complicated, since 5:5'-dichloro-*hydrurilic* is formed as by-product.

Under definite conditions, barbituric acid is converted by bromine and alkali hydroxide into tribromoacetylcarbamide, whereby potassium 5-bromobarbiturate is intermediately produced; the subsequent addition of bromine causes evolution of carbon dioxide and formation of tribromoacetylcarbamide, in accordance with the equation  $C_4H_2O_5N_2BrK + HBrO + Br_2 = C_3H_3O_4N_2Br_3 + CO_2 + KBr$ . Tribromoacetylcarbamide is also obtained from 5:5-dibromobarbituric acid and bromine, but the production of the dibromo-acid is not observed intermediately when barbituric acid is used as initial material.

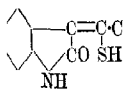
H. W.

**Dyes Derived from Phenanthraquinone. III. Phenanthrazines.** ANUKUL CHANDRA SIRCAR and GOPAL CHANDRA BECAR (T., 1923, 123, 1559—1565).

**The Use of Rhodanine in Organic Syntheses. III. Derivatives of Oxindole.** CH. GRÄNACHER and A. MAHAL (*Helv. Chim. Acta*, 1923, 6, 467—482).—A number of new oxindole derivatives have been synthesised from the condensation product of isatin with rhodanine. According to Andreasch (A., 1917, i, 663), isatin condenses with rhodanine in the 2-position to give "rhodanine-indolindigo," but it is now shown that condensation takes place in the 3-position with formation of 3-rhodanylideneoxindole (annexed formula), which forms a pyridine additive compound,

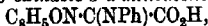


crystallising in red needles. The isomeric  $\psi$ -indoxylidene-rhodanine is obtained by condensing isatin with rhodanine. By warming 3-rhodanylideneoxindole in 10% sodium hydroxide solution, *oxindole-3- $\alpha$ -thiolacetic acid* (annexed formula) is obtained, which forms a bright orange powder. The thiol group is not removed by long boiling with ammonia. The isomeric  $\psi$ -indoxylidene-

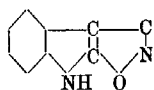


*thiolacetic acid* forms a reddish-brown powder which begins to decompose at  $148^\circ$ . When oxindole-3- $\alpha$ -thiolacetic acid is reduced with zinc and concentrated hydrochloric acid, *oxindole-3-acetic acid* is formed, colourless needles, m. p.  $218-219^\circ$ . Only traces of skatolecarboxylic acid could be obtained by further reduction with sodium and amyl alcohol. By acetic anhydride, oxindole-3-acetic acid is converted into *diacetyloxindole-3-acetic acid* (*N-acetyloxindole-3-acetic anhydride*), lustrous leaflets, m. p.  $228-230^\circ$ . By heating with aniline, oxindole-3- $\alpha$ -thiolacetic acid is converted into *aniline*  $c^*$

*oxindole-3- $\alpha$ -aniloacetate*, yellow needles, m. p. 232°, sintering from 220°. The free *oxindole-3- $\alpha$ -aniloacetic acid*,



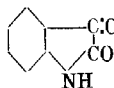
forms a yellow, crystalline powder, m. p. 232°. The *silver salt*, which forms bunches of needles, is decomposed by water. *Oxindole-3-glyoxylic acid* is obtained by hydrolysis of the above aniline salt in boiling acetic acid solution, and crystallises in orange leaflets, decomposing at 265–270°. Its ammoniacal solution reduces a solution of a silver salt. By the action of hydroxylamine on oxindole-3- $\alpha$ -thiolacetic acid there is formed, not the expected oximino-



compound, but *indoisoxazole- $\gamma$ -carboxylic acid* (annexed formula) by the closure of an isoxazole ring. The compound crystallises in yellow cubes or lustrous, yellow leaflets, m. p. 251°. When the ammonium

salt of this acid reacts with silver nitrate, the *silver oxindole-3- $\alpha$ -oximinoacetate* is formed, crystallising in yellowish-white needles.

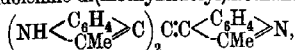
*N*-Methylisatin condenses with rhodanine to form *3-rhodanylidene-N-methyloxindole*, crystallising in red needles. By alkali, it is converted into the corresponding  $\alpha$ -thiolacetic acid.



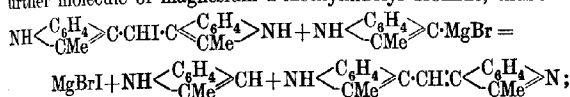
The oxindole-3-aldehyde described by Friedländer (A., 1910, i, 592) does not condense with rhodanine, probably because it is not a true aldehyde, but has the tautomeric acid-structure (annexed formula). This is confirmed by the strongly acid properties of the aldehyde. With benzene-sulphonyl chloride, it forms a *phenylsulphonoxindole-3-aldehyde*, (annexed formula) brownish-yellow needles, m. p. 155–160° (decomp.); and with benzoyl chloride it gives *benzoyloxindole-3-aldehyde*, yellow needles, m. p. 192°. E. H. R.

**The Action of Potassium Hydroxide on Chloroacetyl-*p*-anisidine.** FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1923, 6, 424–428).—Although nitro-derivatives of chloroacetyl-*p*-anisidine are readily hydrolysed by dilute alkali hydroxides, in the case of chloroacetyl-*p*-anisidine itself very little *p*-anisidine is formed, but condensation products arise, differing according to the solvent used. With aqueous 4% potassium hydroxide on the water-bath, a compound is formed, m. p. 185–186°, crystallising in white needles, having the composition  $\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_2$  or  $\text{C}_{12}\text{H}_9\text{O}_5\text{N}_2$ , and a second compound, m. p. 133°. The first compound gives with lead peroxide in acetic acid solution a blue coloration, changing through violet to brown; it can be sulphonated, and with nitrous acid forms a derivative, yellow needles, m. p. 168°, which may be a nitro-derivative. With alcoholic potassium hydroxide, chloroacetyl-*p*-anisidine gives a crystalline product, m. p. 257–258°, needles, which does not give a coloration with lead peroxide, and appears to be 2:5-diketol-1:4-di-*p*-anisylpiperazine. It forms a *tetranitro*-derivative, m. p. 282–283° (decomp.). E. H. R.

**Syntheses in the Indole Group. IX. Indyl Colouring matters derived from Methane.** BERNARDO ODDO and RANCESCO TOGNACCHINI (*Gazzetta*, 1923, 53, i, 271—275).—The action of magnesium 2-methylindolyl bromide on iodoform yields an orange-yellow compound, m. p. 231—232°, which imparts its colour to wool and silk and yields a leuco-base on reduction. According to the simplest interpretation of the reaction, this leuco-base would have the formula  $(\text{NH} \langle \text{C}_6\text{H}_4 \rangle_{\text{CMe}} \text{C})_3\text{CH}$ , and would give on oxidation 2-methylindolenine-di(methylindolyl)methane,



which would be identical with the compound obtained by Ellinger and Flamand (A., 1909, i, 846; 1911, i, 329). Since, however, the interaction of iodoform and magnesium phenyl bromide yields principally tetraphenylethane (cf. Oddo and Binaghi, A., 1922, 52, 313), it is probable that the first product of the above reaction is 2-iododi-methylindolyl-methane, and that this then reacts with a further molecule of magnesium 2-methylindolyl bromide, thus:



the final product would then be 2-methylindolyl-2-methylindolidene-methane. Alternatively, the latter might be formed by auto-oxidation of tetra-2-methylindolylethane, which possibly constitutes the first product of the reaction.

The tartrate of the orange-yellow base,  $\text{C}_{19}\text{H}_{16}\text{N}_2 \cdot \text{C}_4\text{H}_6\text{O}_6$ , m. p. 167°, and the sulphate (cf. Ellinger and Flamand, *loc. cit.*) were analysed.

T. H. P.

**Preparation of certain Azo-derivatives.** DINO BIGIARI and GINO CARRARA (*Gazzetta*, 1923, 53, i, 285—290; cf. A., 1922, i, 878).

The authors have prepared various azoxyphenols by the action of acetic acid and hydrogen peroxide on the corresponding azo-derivative, and various nitro-derivatives of azo-compounds by treating the latter with nitrous acid. When the residue  $\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$  is present, this reagent, even in marked excess, yields a mono-nitro-derivative with the nitro-group in the ortho-position to the hydroxyl, whereas the radicals  $\text{NPh}$ ,  $\text{NO} \cdot \text{Ph}$ , and  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$  are inert towards nitrous acid. In this way, it is therefore possible to establish the position of the azo-oxygen in the azoxyphenols,  $\alpha$ -azoxyphenol yielding a nitro-derivative, and  $\beta$ -azoxyphenol remaining unchanged, when treated with nitrous acid. A quantitative yield of nitro-derivative is obtained with the azoxyphenols but not with the azophenols. *p*-Azophenol is partly oxidised to *p*-nitrophenol by the action of nitrous acid, this reaction being analogous to the oxidation of hyponitrous acid to nitric acid by the action of permanganate in alkaline solution.

The yield of *p*-azophenol may be raised from 36—42% to 60—

cc\* 2

70% by varying the procedure given by Willstätter and Benz (A., 1906, i, 990).

*p*-Azoxyphenol forms lustrous, reddish-yellow needles, m. p. 224° (decomp.), a molecule of water of crystallisation being lost at 100°; Fischer and Wacker's preparation (A., 1888, 1286) was impure.

Diacetyl-*p*-azoxyphenol has m. p. 163° (Wohl and Goldenberg, A., 1904, i, 210, gave m. p. 165°).

$\alpha$ -*m*-Nitro-*p*-hydroxyazoxybenzene,  $\text{C}_6\text{H}_5\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NO}_2$ , forms transparent, greenish-yellow, tabular crystals, m. p. 125°.

*m*-Nitro-*p* : *p*'-dihydroxyazoxybenzene,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NO}_2$ , crystallises in reddish-yellow chips, m. p. 193° (decomp.).

When treated with nitrous acid, *p*-azophenol yields the *m*:*m*'-dinitro-derivative (Robertson, T., 1913, 103, 1473), together with *p*-nitrophenol and a black, pulverulent compound, m. p. 174° (decomp.), corresponding in composition with Willstätter and Benz's azoquinhydrone (*loc. cit.*). T. H. P.

**Hydrochlorides of *p*-Aminoazo-compounds.** D. VOELANDER and ERNST WOLFERTS (*Ber.*, 1923, 56, [B], 1229—1230).—The addition of hydrogen chloride to a number of *p*-aminoazo-compounds under widely varied conditions has been examined. The observations are not readily explicable by the hypothesis that quinonoid compounds are produced.

The following salts of *p*-dimethylaminoazobenzene are described: the anhydrous *monohydrochloride*, from equivalent quantities of base and hydrogen chloride in anhydrous ether, dark, reddish-violet crystals, m. p. 168—174°, or black to brownish-red crystals, m. p. 162—167°, decomp. about 173°, prepared by passing dry air over the hydrated monohydrochloride or the dihydrochloride: the anhydrous *dihydrochloride*, m. p. about 162°, decomp. about 173°, a pale red or red, crystalline powder obtained by passing dry hydrogen chloride over the anhydrous monohydrochloride at the atmospheric temperature; a mixture of the two hydrochlorides (or a compound of a molar proportion of base with one and a half molar proportions of acid), clusters of red needles, m. p. about 172°, from solutions of the base in anhydrous ether or light petroleum saturated with hydrogen chloride; the monohydrated monohydrochloride, purple-red needles with bluish-violet glance, m. p. 96—105°, decomp. about 115°, from dilute hydrochloric acid; the compound, probably  $\text{C}_{14}\text{H}_{15}\text{N}_3\cdot 2\text{HCl}\cdot 4\text{H}_2\text{O}$ , dark red leaflets, m. p. about 60°, decomp. about 90°, from solutions of the base in hydrochloric acid (*d* 1.1); the *monohydrochloride* (+ $\text{C}_6\text{H}_6$ ), lustrous, red leaflets, m. p. about 165° (decomp.), prepared from the base and hydrogen chloride in the presence of benzene; the *monohydrochloride* (+ $\text{CHCl}_3$ ), lustrous, red needles, m. p. about 166°, decomp. about 175°, from the base and hydrogen chloride in chloroform solution. (The melting and decomposing points depend greatly on the previous history of the specimens and the manner of heating.)

*p*-Aminoazobenzene hydrochloride does not show any tendency

to combine with benzene, chloroform, or ether when formed in the presence of these media. It shows little ability to combine with a further molecule of hydrogen chloride.

The alteration in colour caused by the transformation of the mono- to the di-hydrochloride is more pronounced in the case of *N,N*-dimethylamino-*p*'-methoxyazobenzene, m. p. 161–163°. The *monohydrochloride* is blue or bluish-violet, whereas the *dihydrochloride* is yellowish-red. The transformation can be effected readily in aqueous hydrochloric acid solutions of suitable concentration and reversed by diluting on warming the solution. The hydrogen chloride is less firmly retained than in the case of the corresponding non-methoxylated compound.

*pp'*-Tetramethyldiaminoazobenzene behaves very similarly to *N,N*-dimethylamino-*p*'-methoxyazobenzene. It gives a blue *monohydrochloride*, m. p. about 220°, and a red *dihydrochloride*, m. p. about 190°, which do not contain solvent of crystallisation. Both compounds readily lose hydrogen chloride with the formation of the free base. At the atmospheric temperature, the red *dihydrochloride* combines further with hydrogen chloride, whereby its colour becomes only slightly paler.

H. W.

#### A Drop Method for the Study of the Coagulation of Proteins.

AN BRČKA (*Biochem. Z.*, 1923, 137, 456–464).—To save time, labour, and material involved in making large numbers of dilutions in test-tubes of reagents and proteins, the author uses a glass plate with black undersurface. By means of a capillary tube drops of the previously prepared dilutions can be placed rapidly and systematically on the plate and mixed with drops of the suitably diluted precipitant. A glance shows the limits of coagulation at the different dilutions.

H. K.

**The Structure of Proteins.** EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 128, 119–128).—Diketopiperazine compounds have been isolated from the hydrolysis of protein. Silk fibrin when hydrolysed with 70% sulphuric acid yields *glycylalanine anhydride*,  $C_4H_6O_4N_2$ , m. p. 247°,  $[\alpha]_D^{20} -4.7^\circ$  (2% solution in water). Casein yields *l-leucyl-d-valine anhydride*,  $C_{11}H_{20}O_4N_2$ ,  $[\alpha]_D^{20} -45.9^\circ$  (in acetic acid), and also *l-phenylalanyl-d-alanine anhydride*. From diadin, in the same way, *l-prolyl-l-leucine anhydride*, m. p. 160°,  $[\alpha]_D^{20}$  about  $-120^\circ$  (in alcohol), and *l-prolylglycine anhydride*, m. p. 169°,  $[\alpha]_D^{20} -206.5^\circ$  (in water), were obtained. The structure of proteins is discussed in the light of these findings, particularly with regard to the possibility of the existence of such diketopiperazine rings in the protein molecule.

W. O. K.

#### Protein Chemistry. III. Iodination of Proteins with Nitrogen Iodide.

F. BLUM and E. STRAUSS (*Z. physiol. Chem.*, 1923, 127, 199–207).—By the action of iodine in ammoniacal solution in the cold on proteins, iodoproteins are obtained which give the biuret reaction and are more closely allied to the original protein than iodoproteins previously obtained. That from serum albumin contains 6.6% of iodine, that from ovalbumin 5.2%, and that from thyroglobulin 4.8%.

W. O. K.

**Partial Decomposition of Protein.** EMIL ABDERHALDEN and HIDEKI SUZUKI (*Z. physiol. Chem.*, 1923, 127, 281—290).—Goose feathers were allowed to remain five days at room temperature with ten times their weight of 70% sulphuric acid, and the mixture then poured into water. The products of hydrolysis were fractionated. A product,  $C_{17}H_{26}O_5N_4$ , has been isolated which is apparently polypropylglycylglycylprolyl,  $[\alpha] -147.5^\circ$ .

W. O. K.

**The Rotation and Molecular Weight of Casein.** J. ZAYKOWSKY (*Biochem. Z.*, 1923, 137, 562—569).—The rotation of pure casein prepared by avoiding the action of hydroxyl-ions has been examined under a variety of conditions. A 1% solution in 10% potassium acetate has  $[\alpha]_D^{25} +81.55^\circ$ ; somewhat higher values are found in sodium acetate and sodium salicylate solutions, and also with increasing concentration of the casein. Warming in neutral solution has no influence on the rotation. In alkaline solutions, the rotation falls off and especially rapidly on warming at  $80^\circ$ . Various concentrations of borax have no influence on the rotation of 2% casein solution ( $[\alpha]_D^{25} +95.3^\circ$ ). In *N*/10-hydrochloric acid the rotation was  $88.97^\circ$ . When increasing volumes of *N*/10-sodium, potassium, calcium, or barium hydroxides are added to casein, the rotation increases to a maximum at 8.0 c.c. per 0.25 g. of casein. This corresponds with 0.0032 g. equivalents of alkali per g. of casein, whereas 1 g. of casein requires 0.0008 g. equivalent of alkali to render it neutral to phenolphthalein. If the latter point corresponds with a bi-metallic salt, then casein is an octabasic acid and has a molecular weight of about 20,000.

H. K.

**Hæmatoidin.** HANS FISCHER and FRITZ REINDEL (*Z. physiol. Chem.*, 1923, 127, 299—316).—From a study of the crystallographic and general properties of hæmatoidin,  $C_{33}H_{36}O_6N_4$ , it is concluded that it is identical with bilirubin. Both give similar compounds on coupling with diazo-salts.

W. O. K.

**Bile Pigments. VII.** HANS FISCHER and GEORG NIEMANN (*Z. physiol. Chem.*, 1923, 127, 317—328).—If bilirubin is reduced with hydrogen and palladium, mesobilirubin is obtained (cf. A. 1914, i, 1135; 1915, i, 148) of which the dimethyl ester, hydrochloride,  $C_{34}H_{44}O_6N_4 \cdot 2HCl$ , lustrous, green leaflets, red by transparent light, m. p.  $190^\circ$ , is now described. On further reduction, mesobilirubin yields mesobilirubinogen, m. p.  $202^\circ$ . A colloidal solution of mesobilirubin is formed when a mixture of mesobilirubin (0.1 g.) and taurocholic acid (0.1 g.) is dissolved in alkali and precipitated with acid. This colloidal solution fluoresces strongly. Mesobilirubin, when treated with concentrated nitric acid, yields methylethylmaleimide.

W. O. K.

**Synthetic Researches on the Constitution of Bile Pigments.** I. HANS FISCHER and ERNST LOY (*Z. physiol. Chem.*, 1923, 128, 59—84).—From ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate, on treatment with anhydrous hydrocyanic acid and hydrochloric acid in chloroform solution, is formed the corresponding aldimine,

$\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_2$ , brown needles, m. p.  $235^\circ$ , which is hydrolysed with dilute sodium hydroxide solution to yield *ethyl 4-hydroxy-2-aldehydro-2-methylpyrrole-3-carboxylate*, pale yellow needles, m. p.  $187^\circ$ ; *semicarbazone*, yellow leaflets, decomp.  $243^\circ$ ; *oxime*, colourless needles, m. p.  $202^\circ$ ; *acetyl derivative* of the oxime,  $\text{C}_{11}\text{H}_{14}\text{O}_5\text{N}_2$ , yellow needles, m. p.  $115^\circ$ ). If the aldimine or the free aldehyde is heated on the water-bath with dilute acid, condensation takes place and *bis-(4-hydroxy-3-carbethoxy-2-methylpyrrol)methene*,  $\text{C}_{11}\text{H}_{20}\text{O}_6\text{N}_2$ , is formed, yellow needles, decomp.  $240-275^\circ$ . The aldehyde also condenses with ethyl 2:4-dimethylpyrrole-3-carboxylate to yield (4-hydroxy-3-carbethoxy-2-methylpyrrol-2:4-dimethyl-3-carbethoxypyrrolidyl)methene,  $\text{C}_{18}\text{H}_{22}\text{O}_5\text{N}_2$ , thin, yellow needles, decomp.  $245^\circ$ , which is reduced with hydrogen in presence of platinum black to form (4-hydroxy-3-carbethoxy-2-methylpyrrol-2:4-dimethyl-3-carbethoxypyrryl)methane, pale yellow needles, m. p.  $191^\circ$ . Acetic acid-hydrogen iodide acts on ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate to yield a compound,  $\text{C}_{16}\text{H}_{20}\text{O}_5\text{N}_2$ , colourless leaflets, m. p.  $158^\circ$ , described by Benary and Silbermann (A., 1913, i, 651) and the same compound is formed in attempting to condense the hydroxypyrrrole with acetonitrile in chloroform solution in presence of hydrogen chloride. It is apparently 5-(3-carbethoxy-2-methyl-4-pyrrol)-4-hydroxy-3-carbethoxy-2-methylpyrrole.

Condensation of ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate with formic acid yields the above-mentioned *bis-(4-hydroxy-3-carbethoxy-2-methylpyrrol)methene*, decomp.  $240-275^\circ$ , and also *bis-(2-methyl-3-carbethoxypyrryl)furan*, yellow needles, decomp.  $282^\circ$ . The latter compound is also formed on heating ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate with oxalic acid, and also there is formed in the reaction *bis-(4-hydroxy-3-carbethoxy-2-methylpyrrol)diketone*, yellow needles, m. p.  $245-250^\circ$ . Ethyl oxalate condenses with ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate in presence of sodium ethoxide, and a compound,  $\text{C}_{16}\text{H}_{11}\text{O}_6\text{N}_2$ , fine white needles, decomp.  $201^\circ$ , which is apparently 4-hydroxy-3-carbethoxy-2-methylpyrrol-5-pyruvic acid, is obtained. Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate and chloroacetonitrile condense in ethereal solution in presence of hydrogen chloride to form *ethyl 4-hydroxy-5-chloroacetyl-2-methylpyrrole-3-carboxylate*, thin white needles, decomp.  $243^\circ$ .

The compound formed by the condensation of ethyl 5-aldehyde-2:4-dimethylpyrrole-3-carboxylate with ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate, is (3-carbethoxy-2:4-dimethylpyrrol-4-hydroxy-3-carbethoxy-2-methylpyrrolidyl)methene, which forms orange-yellow leaflets from alcohol, which decompose at  $244^\circ$  (hydrochloride, orange-red needles, m. p.  $207^\circ$ ). This compound, on reduction with hydrogen in presence of platinum, yields 4-hydroxy-3-carbethoxy-2-methylpyrrol-3-carbethoxy-2:4-dimethylpyrrylmethane, already mentioned as being formed by the reduction of the isomeric methene compound. Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate similarly condenses with (a) ethyl 4-aldehyde-1-p-tolyl-2:5-dimethylpyrrole-3-carboxylate to yield a compound,

$C_{25}H_{28}O_5N_2$ , yellow leaflets, m. p.  $211^\circ$ , which is again decomposed on coupling with diazobenzene sulphonic acid, (b) ethyl 4-aldehyde-2:5-dimethylpyrrole-3-carboxylate to yield a compound, yellow, glistening leaflets, m. p.  $240^\circ$ , and (c) with ethyl 4-aldehyde-1-phenyl-2:5-dimethylpyrrole-3-carboxylate to yield a compound, microscopic needles, decomp.  $210^\circ$ .  
W. O. K.

**I. Nucleotides Formed by the Action of Boiled Pancreas on Yeast-nucleic Acid. II. Formation of Nucleotides from Yeast-nucleic Acid by the Action of Sodium Hydroxide at Room Temperature.** WALTER JONES and M. E. PERKINS (*J. Biol. Chem.*, 1923, 55, 557—565, 567—568).—The authors have now isolated the four nucleotides from the product of the action of boiled pancreas extract on yeast-nucleic acid (cf. A., 1920, i, 687; 1922, i, 479; Levene, A., 1921, i, 821); incidentally, the acid brucine salt of guanine nucleotide has been obtained in a crystalline form, and a crystalline compound which is probably the lead ammonium salt of cytosine nucleotide has been isolated. The decomposition of the nucleic acid into its constituent nucleotides is, however, by no means complete; intermediate substances are present in the final product. It is considered that only nucleotide linkings are ruptured by the action of the thermostable agent from pig's pancreas, and, since there is no increase in the titratable acidity of the mixture during the process, the conclusion is drawn that at least one nucleotide linking is of the ether type between the carbohydrate groups. Conditions have, however, been devised whereby yeast-nucleic acid is apparently quantitatively decomposed into its mononucleotides by the action of 1% sodium hydroxide at the ordinary temperature, and in this case the alkalinity of the solution has been observed to diminish progressively as the decomposition proceeds, thus indicating the liberation of weak acids during the formation of the nucleotides. From this result it is concluded that one or more of the nucleotide linkings in nucleic acid are between a phosphoric acid and a carbohydrate group. A new formula is consequently proposed for yeast-nucleic acid in which two such linkings are present, the third being of the ether type mentioned above.  
E. S.

**The Action of Alkali on Thymus-nucleic Acid and Yeast-nucleic Acid.** H. STEUDEL and S. NAKAGAWA (*Z. physiol. Chem.*, 1923, 128, 129—134).—The rotatory power of thymus-nucleic acid obtained from herring sperm or from spleen is not influenced by remaining several days with alkali, whereas that of yeast-nucleic acid changes from dextro to lævo. Natural or synthetical clupein nucleate, when left with alkali shows only a small decrease in its levorotation. This small change is probably to be ascribed to the protein portion. Sodium guanylate undergoes a small change in rotation when left in contact with hydrochloric acid.  
W. O. K.

**Yeast-nucleic Acids. IV. A Simple Method of Isolating Adenylic Acid.** H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1923, 127, 262—267).—After separation of guanylic acid as the

sodium salt (A., 1922, i, 279), adenylic acid may be isolated from yeast by precipitation as the lead salt. Adenylic acid, m. p.  $195^{\circ}$ ,  $[\alpha]_D^{20} = -41.78^{\circ}$ , has the formula  $C_{10}H_{14}O_7N_5P, H_2O$ . W. O. K.

**Fission of Proteins by Formic Acid.** N. D. ZELINSKY and V. S. SADIKOV (*Biochem. Z.*, 1923, **137**, 397—400).—Formic acid of various strengths proved unsuitable for the hydrolysis of proteins even using an autoclave at  $180^{\circ}$ . Examination of the products of the action of 10% formic acid on gelatin only gave one amino-acid, glycine. Even after hydrolysis with hydrochloric acid, the products are very complex. Formic acid appears to effect condensation. H. K.

**Relation between the Fermentative and Catalytic Fission of Proteins.** VLADIMIR SERGIEVITSCH SADIKOV and N. D. ZELINSKY (*Biochem. Z.*, 1923, **137**, 401—404).—There is a rough parallelism between the proportion of ether, chloroform, and ethyl acetate soluble extracts from the catalytic fission (1% phosphoric acid at  $180^{\circ}$ ) and from the fermentative fission (pepsin, trypsin, and erepsin) of gelatin and casein indicating similarity of the chemical processes involved. H. K.

**The Specificity of Enzymes. III. The Affinity of Enzymes for Stereoisomeric Sugars.** RICHARD WILLSTÄTTER and RICHARD KUHN (*Z. physiol. Chem.*, 1923, **127**, 234—242).—The effect of  $\alpha$ - and  $\beta$ -glucose on the rate of inversion of sucrose by invertase has been compared.  $\alpha$ -Glucose causes no change in  $k$ , the velocity constant of the reaction, but  $\beta$ -glucose causes a decrease from 158.5 to 137.5. A similar difference between the effects of  $\alpha$ - and  $\beta$ -glucose is observed in the case of the hydrolysis of raffinose by invertase. In the case of maltase, however, acting on maltose, both  $\alpha$ - and  $\beta$ -glucose have approximately the same effect,  $\beta$ -glucose being at most only slightly more effective than  $\alpha$ -glucose. The enzymes of the emulsin complex in their action on salicin and helicin, are, like invertase, inhibited to a greater degree by the addition of  $\beta$ -glucose than of  $\alpha$ -glucose. W. O. K.

**Saccharase. II.** H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, **56**, [B], 1097—1103).—The purest saccharase preparations which have been obtained resemble closely the natural proteins in their chemical nature. The nitrogen content, which increases with increasing purity of the enzyme, is of the same order of magnitude as the mean value found for the proteins, and it is probable that an eventual, not very considerable, increase in the purity of the enzyme would cause the disappearance of the observed difference. The amino-nitrogen is only a small fraction of the total nitrogen. Hydrolysis of saccharase with concentrated acids increases the number of free amino-groups in the same manner as in the case of the natural proteins. It appears highly probable that purified saccharase preparations have a sulphur content which is proportional to their activity; the order of magnitude is identical with that exhibited by the proteins. The preparations of saccharase ( $f = 100$ —230), therefore, appear to consist largely of substances which

are closely allied to the proteins. This hypothesis is in harmony with their change in thermostability with temperature. H. W.

**Emulsin.** II. BURCKHARDT HELFERICH, PAUL ELIAS SPEIDEL, and WALTER TOELDT (*Z. physiol. Chem.*, 1923, **123**, 99—108).—The activity of emulsin is reduced by the action on it of pepsin or by keeping it under methyl alcohol. Ultra-filtration under pressure does not cause much decrease in its activity. Methylation with diazomethane or acetylation with acetyl chloride inactivates it.

W. O. K.

**The Action of Emulsin on the System Hydrocyanic Acid-Benzaldehyde-Benzaldehydecyanohydrin.** E. NORDEFELDT (*Biochem. Z.*, 1923, **137**, 489—495).—The velocity of fission of benzaldehydecyanohydrin is independent of the presence of emulsin and depends solely on the acidity of the solution. The *d*-cyanohydrin is formed (shown previously) in the presence of emulsin more rapidly than the *lævo*-form and is now found to undergo fission more rapidly, resulting in a preponderance of the cyanohydrin.

H. K.

**Reversibility of the Action of Urease of Soja Bean.** HERBERT DAVENPORT KAY (*Biochem. J.*, 1923, **17**, 277—285).—Carbamide is produced in very small quantities during the action of urease on a mixture of ammonium carbonate and carbamate in strong solution in water at room temperatures under conditions which preclude its formation by any other means than enzymic synthesis. The action of urease is therefore reversible. The methods used for the estimation of the synthesised carbamide were the hydrolysis of the compound with urease and consequent estimation of the hydrogen-ion concentration, and the xanthlydrol method. S. S. Z.

**Histozyne.** I. I. A. SMORODINCEV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 156—177).—Histozyne is found in the greatest quantities in the kidneys of pigs and the skeletal muscles of dogs. All the organs of dogs examined, namely, the liver, kidneys, spleen, lungs, and cardiac and skeletal muscles, have the property of hydrolysing hippuric acid with the production of benzoic acid and glycine; the histozyne content being smallest in the liver. This enzyme is also found in the kidneys of calves and horses. The best sterilisers for histozyne are sodium fluoride or toluene. A number of experiments carried out with this enzyme on the hydrolysis of hippuric and other substituted amino-acids show that it is almost insoluble in water or aqueous glycerol, and must therefore be considered as an endo-ferment. Its activity is not very pronounced, being greatest for hippuric acid with a 4% emulsion, the rate of hydrolysis being greatest at the beginning of the reaction, and then slowly decreasing. With more dilute solutions of hippuric acid the percentage hydrolysis is greater than for more concentrated solutions. Chloroform, phosphates, physiological salt solution, and alkalis have a retarding influence on the hydrolysis, the presence of only 0.004% of sodium hydroxide having a marked effect. Sulphuric acid, on the other hand, accelerates the reaction. At 8°, histozyne exhibits

a feeble hydrolytic action on hippuric acid, whilst at 37° its action is four times as great as at 15°. It has no action on  $\beta$ -alanine, *d*-,  $\beta$ -benzamido-*isobutyric*, benzamido-*isobutyric*, and *L*- $\alpha$ -benzamido-*butyric* acids, but is capable of hydrolysing *d*- $\alpha$ -benzamido-*butyric* acid, and *L*-leucine, with the liberation of benzoic acid, and glycocholic and taurocholic acids with the liberation of cholic acid. Histozyyme is also probably the ferment responsible for the hydrolysis of laurylglycine, laurylalanine, laurylalanineglycine, butyrylglycine, and butyrylalanine with the production of the corresponding fatty acids. In view of the above reactions, it is thought desirable that histozyyme should be renamed "aminoacylase," in order to bring its name into line with those of other ferments.

R. T.

**Histozyyme. II.** I. A. SMORODINCEV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 173—182).—A preparation of histozyyme from the kidneys of dogs has only half the hydrolytic power of the juice expressible from them, whilst from the liver, the latter is six times less active than a preparation made from the organ itself. More of the ferment is contained in the kidneys of dogs than in those of oxen, or than in the liver of dogs. The precipitation of histozyyme from the expressed juice by means of acetone slightly reduces its activity, as does the prolonged action of ether. Autolysis greatly reduces the hydrolytic power of the juice, and to a lesser extent that of the preparation of histozyyme obtained from the latter by precipitation with acetone.

R. T.

**Oxidising Enzymes. VI. Tyrosinase.** MURIEL WHELDALE UNSLOW (*Biochem. J.*, 1923, **17**, 216—219).—In corroboration and extension of Bach's hypothesis that tyrosinase consists of at least two enzymes (A., 1914, i, 445) the author puts forward a suggestion that this enzyme is a mixture of a water-splitting enzyme (reductase or deaminase), a carboxylase, and an oxydase.

S. S. Z.

**The Influence of Thorium-X on the Catalase of Liver.** ALFRED MAUBERT, LÉON JALOUSTRE, and PIERRE LEMAY (*Compt. rend.*, 1923, **176**, 1502—1505).—The presence of thorium-X affects the action of the catalase of liver on hydrogen peroxide, activating it when present in small quantities, but inhibiting it if the quantities are increased beyond a certain point. This is apparently due to the  $\alpha$ -radiation, as thorium emanation has a similar effect.

H. J. E.

**Enzymic Fat Synthesis. II.** L. SPIEGEL (*Z. physiol. Chem.*, 1923, **127**, 208—209; cf. A., 1922, i, 694).—The addition of calcium chloride increases the yield of fat obtained from glycerol and fatty acids by the action of an enzyme emulsion prepared from fresh sunflower seeds.

W. O. K.

**The Sulphur Content of Arsphenamine [Salvarsan] and its Relation to the Mode of Synthesis and the Toxicity. IV.** WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, **45**, 1316—1321).—Conclusions previously drawn respecting the distribution of sulphur in salvarsan (A., 1922, i, 601) have been substantiated.

The use of pure instead of commercial sodium hyposulphite for the reduction of 3-nitro-4-hydroxyphenylarsinic acid or the corresponding amino-acid results in a greater rate of reduction, a larger yield and a higher sulphur content. These factors are controlled by the acidity of the reduction mixture, and the addition of sodium carbonate to pure sodium hyposulphite slows down the rate of reduction, decreases the yield, and lowers the sulphur content. The use of acetic acid with commercial hyposulphite has the opposite effect. Specimens of salvarsan prepared by means of pure hyposulphite are more soluble in water than if commercial hyposulphite is used.

W. S. N.

**Arsenated Derivatives of Diketophenylpyrrolidine.** JOSEPH R. JOHNSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 1307—1315).—Details are given of the preparation of nitrophenylarsinic acids by the diazotisation of the corresponding amine and treatment of the diazo-derivative with sodium arsenite solution. *o*-Methoxyphenylarsinic acid, white needles, m. p. 193—194°, is obtained by the use of *o*-anisidine; similarly, *p*-anisidine gives *p*-methoxyphenylarsinic acid. *p*-Nitro-*o*-methoxyphenylarsinic acid, pale yellow needles, m. p. above 250°, is prepared from *o*-methoxy-*p*-nitroaniline, which is formed in 60% yield, together with 5-nitro-2-methoxyaniline (32%), by the action of ice-cold nitric acid on *o*-acetanilide in acetic acid-acetic anhydride solution. *o*-Arsanilic acid, 3-amino-*o*-tolylarsinic acid, 5-amino-*o*-tolylarsinic acid, and *p*-amino-*o*-methoxyphenylarsinic acid, white needles, m. p. 203—204° (203—209°, if heated rapidly), are prepared by the reduction of the corresponding nitro-compounds by means of ferrous chloride. Arsenated derivatives of diketophenylpyrrolidine are produced by boiling pyruvic acid with an alcoholic solution of an aminoarylsaric acid and an aromatic aldehyde, but aminoarylsaric acids having a substituent in the *ortho*-position to the amino-group form benzylidene derivatives which do not react with pyruvic acid. The reaction is not applicable to the simple aliphatic aldehydes. Benzaldehyde, *p*-arsanilic acid, and pyruvic acid (or ethyl pyruvate) give 4 : 5-diketo-2-phenylpyrrolidine-1-*p*-phenylarsinic acid,  $\text{CO}-\text{CO} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$  previously described as 4-carboxy-2-phenylquinoline-6-arsinic acid (A., 1922, i, 187). The quinoline structure was originally assigned to this compound because it loses carbon dioxide on heating. It is now found, however, that 4 : 5-diketo-2-phenyl-1-*p*-nitrophenylpyrrolidine also loses carbon dioxide when boiled with ethyl benzoate, particularly in the presence of an equal quantity of *o*-nitrophenylarsinic acid. Moreover, when the compound is subjected to alkaline fusion, aniline is the chief nitrogenous product. It is held, therefore, that the pyrrolidine structure is firmly established for this compound. Benzylidene-*p*-arsanilic acid, heavy, white, granular crystals, m. p. 225° (decomp.), is formed in small quantities during the preparation. By using *o*-methoxybenzaldehyde in place of benzaldehyde, 4 : 5-diketo-2-*o*-anisylpyrrolidine-1-*p*-phenylarsinic acid is obtained as a pale

yellow powder, m. p. 173—176° (decomp.). Anisaldehyde condenses with arsanilic acid and pyruvic acid to give 4:5-diketo-*p*-anisylpyrrolidine-1-*p*-phenylarsinic acid, white crystals, m. p. 164—165° (decomp.). 4:5-Diketo-2-*mp*-methylenedioxyphenylpyrrolidine-1-phenylarsinic acid, light yellow powder, m. p. 176—178° (decomp.), is formed from arsanilic acid, piperonal, and pyruvic acid, whilst the use of *p*-chlorobenzaldehyde leads to the formation of 4:5-diketo-2-*p*-chlorophenylpyrrolidine-1-*p*-phenylarsinic acid, white powder, m. p. 163—165° (decomp.). Condensation products are also formed from salicylaldehyde, *p*-dimethylaminobenzaldehyde, or cinnamaldehyde, but not from paracetaldehyde or *n*-butaldehyde. 4:5-Diketo-2-phenylpyrrolidine-1-*m*-tolyl-6-arsinic acid, cream-coloured powder, m. p. 180—186° (decomp.), is made from 6-amino-tolylarsinic acid, pyruvic acid, and benzaldehyde; benzaldehyde, pyruvic acid, and *p*-amino-*o*-anisylarsinic acid give 4:5-diketo-2-phenylpyrrolidine-1-*m*-anisyl-4-arsinic acid, yellow powder, m. p. 175—176°. Benzaldehyde condenses in alcoholic solution with arsanilic acid to give benzylidene-*o*-arsanilic acid, m. p. 228—230° (decomp.), and with *m*-methyl-6-amino-*m*-tolylarsinic acid with formation of 6-benzylideneamino-*m*-tolylarsinic acid, cream-coloured solid, m. p. 202—205° (decomp.). *p*-Chlorobenzaldehyde and 6-amino-tolylarsinic acid give 6-*p'*-chlorobenzylideneamino-*m*-tolylarsinic acid, pale yellow powder, m. p. 255—260° (decomp.). The same benzylidene derivatives are produced in the presence of pyruvic acid.  
W. S. N.

**Mercury Compounds of the Phenyl Halides.** MARTIN E. LANKÉ (*J. Amer. Chem. Soc.*, 1923, 45, 1321—1330).—Halogenated phenylsulphinic acids, prepared by a modification of Gattermann's method (A., 1899, i, 516), react with mercuric acetate in acetic acid solution with formation of halogen derivatives of phenylmercuric acetate, which are converted by means of aqueous alcoholic sodium chloride into derivatives of phenylmercuric chloride. By the action of bromine in an aqueous suspension containing potassium bromide, or, perhaps better, by means of bromine in acetic acid solution, the mercuric acetate grouping is replaceable by bromine.

The following compounds are described: *p*-Chlorophenylmercuric acetate, m. p. 193°, is prepared from *p*-chlorobenzene-sulphinic acid; the corresponding chloride has m. p. 225°. *m*-Chlorobenzene-sulphinic acid, long, white needles, m. p. 81°. *m*-Chlorophenylmercuric acetate has m. p. 133°; the chloride, m. p. 210°. Chlorobenzene-sulphinic acid is a white, crystalline solid, m. p. 20°. *o*-Chlorophenylmercuric acetate has m. p. 115°; the chloride, m. p. 145°. *p*-Bromophenylmercuric acetate has m. p. 196°; the chloride, m. p. 250°. *m*-Bromobenzene-sulphinic acid, m. p. 88°. *p*-Bromophenylmercuric acetate, m. p. 160°, and the chloride, m. p. 38°. *o*-Bromobenzene-sulphinic acid, m. p. 130°. *o*-Bromophenylmercuric acetate, m. p. 124°, and the chloride, long, white needles, m. p. 155°. *p*-Iodophenylmercuric acetate, m. p. 191°. All these mercury compounds are white, crystalline solids. The action of

warm 68% nitric acid on *p*- or *o*-chloro-, or *p*- or *o*-bromo-phenyl mercuric acetate leads to the replacement of the mercuric acetate group by the nitro-group, with formation of known products but this reaction does not proceed smoothly with the meta-substituted derivatives. Direct mercuration of phenyl halides may be effected by heating mercuric acetate with a large excess of a phenyl halide at 140° during one and a half to two and a half hours, after which the excess of phenyl halide is removed by distillation in steam. It is shown that in this way *p*-chloro- and *p*-iodo-phenyl mercuric acetates and *o*-, *m*-, and *p*-bromophenylmercuric acetates are produced (cf. Dimroth, A., 1902, i, 656; Kharasch and Jacobsohn, A., 1922, i, 189).

W. S. N.

**Mercury Derivatives of Salicylaldehyde and the Nitrosalicylaldehydes.** FRANK C. WHITMORE and EDMUND BURRIS MIDDLETON (*J. Amer. Chem. Soc.*, 1923, 45, 1330—1334).—The direct mercuration of salicylaldehyde (cf. Henry and Sharp, T., 1922, 121, 1055) is accomplished by boiling with mercuric acetate and a small amount of acetic acid in 50% alcoholic solution, and leads to the formation of 3:5-diacetoxymercurisalicylaldehyde, needles, m. p. 234° (decomp.). This diacetate is soluble in aqueous sodium hydroxide solution; the action of boiling alcoholic potassium iodide removes all the mercury as potassium mercuric iodide, forming salicylaldehyde and potassium hydroxide. The diacetate reacts with hydroxylamine and with phenylhydrazine as an oxidising agent, forming metallic mercury. The action of aqueous sodium chloride gives 3:5-dichloromercurisalicylaldehyde, m. p. above 270°. The same diacetate is also formed in aqueous solution, together with monomercured products; addition of sodium chloride to the filtered product gives 3(?)-chloromercurisalicylaldehyde, m. p. 189—190°, which reacts with iodine in chloroform solution, giving (?)3-iodosalicylaldehyde. 5-Chloromercurisalicylaldehyde is also probably formed. The mercuration of 5-nitrosalicylaldehyde gives 5-nitro-3-acetoxymercurisalicylaldehyde, pale yellow crystals, m. p. above 260°, which dissolves in aqueous sodium hydroxide, giving a solution from which 5-nitro-3-chloromercurisalicylaldehyde, m. p. above 260°, is precipitated by addition of hydrochloric acid. 3-Nitro-5-acetoxymercurisalicylaldehyde, m. p. above 260°, is produced by the mercuration of 3-nitrosalicylaldehyde. Schiff bases are obtained by heating the mercured salicylaldehydes with an excess of aniline or *p*-toluidine; similar compounds are obtained from the aminobenzoic acids in alcoholic or acetic acid solution. 3:5-Diacetoxymercurisalicylalaniline is a brick-red, amorphous, insoluble, infusible product. 3:5-Diacetoxymercurisalicylal-*p*-toluidine, 3:5-diacetoxymercurisalicylal-*p*-aminobenzoic acid, and 3:5-diacetoxymercurisalicylal-*o*-aminobenzoic acid are similar to the aniline compound. 3(?)-Chloromercurisalicylal-aniline forms flat, yellow, insoluble plates, m. p. 182—184°. The action of aniline on 5-nitrosalicylaldehyde-3-mercuric acetate gives the anhydride of 3-hydroxymercuri-5-nitrosalicylalaniline as a dark red, amorphous, infusible product, insoluble in organic solvents,

not soluble in aqueous alkali. In the formation of this compound, the molecule of acetic acid is eliminated, probably between the nitro- and acetoxymercuri-groups. A similar product is obtained from aniline and 3-nitrosalicylaldehyde-5-mercuric acetate. 5-Nitro-chloromercurisalicylatylaniline is an insoluble, infusible, orange-red product.

W. S. N.

### Physiological Chemistry.

**Respiratory Exchange in Fresh-water Fish. VI. Pike (*Esox lucius*).** JOHN ADDYMAN GARDNER and GEORGE KING (*Biochem. J.*, 1923, 17, 170—173).—The oxygen consumed by the pike is approximately proportional to the rise in temperature. This fish can exist at a tension of dissolved oxygen (0.96% of an atmosphere) considerably below normal. When the temperature of water in which the pike is kept is raised, no signs of discomfort are observed until the temperature reaches 27°, when the respirations become markedly deeper, and the fish becomes more active. At about 30°, the movements of the fish become slightly convulsive and it turns over. On return to the outside tank, the pike quickly revives without manifesting any ill effects. S. S. Z.

**The Immediate Effect of Heavy Exercise (Stair-running) in some Phases of Circulation and Respiration in Normal Individuals. III. Effect of Varying the Amount and Kind of Exercise.** CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1923, 55, 599—603).—The decreased oxygen content of blood from the cubital vein, caused by fast stair-running (his vol., i, 502, 623), is not produced by the following types of exercise: (a) walking up and down stairs, (b) riding a bicycle for about two minutes, (c) weight lifting.

E. S.

**The Action of Acetylene. II. Solubility of Acetylene in Water and Blood.** RUDOLF SCHOEN (*Z. physiol. Chem.*, 1923, 17, 243—259).—Acetylene dissolves in the blood according to Henry's law, and its presence in the blood does not influence the solution of oxygen any more than does the presence of nitrogen. The solubility in blood is 98.8% that in water, and the solution appears to be purely physical in nature.

W. O. K.

**Effect of Insulin on Blood-sugar Concentration.** L. B. INTER and W. SMITH (*Nature*, 1923, 111, 810—811).—The blood of rabbits which have received insulin injections and have been bled when the blood-sugar concentration, as estimated by Bang's method, reaches 0.05%, contains a dextrorotatory carbohydrate which is without copper-reducing power. The liver and muscles hold a substance similar to that present in blood. It is suggested that the carbohydrate content of the animal body may not be appreciably diminished after large doses of insulin, and that the

sugar stored as glycogen is converted into this peculiar form, which may possibly be the "intermediate carbohydrate" postulated by Laquer. A. A. E.

**Effect of Plant Extracts on Blood-sugar.** J. B. COLLIE (*Nature*, 1923, 111, 571).—A test of the prediction that whenever glycogen occurs in nature a substance similar to "insulin" would also be found, has given positive results in the case of clam-tissue and yeast. Extracts of onion tops, onion roots, barley roots, and sprouted grain, green wheat leaves, bean tops, and lettuce were found to produce hyperglycemia in rabbits. In the case of yeast, coincident priority is claimed with Winter and Smith. A. A. E.

**Forms of Uric Acid in the Blood.** M. P. WEIL and GUILLAUMIN (*Paris Medical*, 1922, 12, 588; *J. Amer. Med. Assoc.*, 1923, 80, 729).—In addition to the free uric acid and urates estimated by the usual methods, more or less complete remnants of nucleotides are present. Free uric acid is present in both plasma and corpuscles; the latter also contain the combined form. A method of estimation is described.

#### CHEMICAL ABSTRACTS.

**Distribution of Ions in Serum.** P. RONA and H. PETROW (*Biochem. Z.*, 1923, 137, 356—363).—When serum is dialysed at different hydrogen-ion concentrations the sodium-, chlorine-, and calcium-ions become distributed according to Donnan's theory. The potassium-ion is anomalous and this is attributed to the formation of a non-ionisable complex with the protein. H. K.

**A Possible Factor Influencing the Assimilation of Calcium.** CHARLES H. HUNT, A. R. WINTER, and R. C. MILLER (*J. Biol. Chem.*, 1923, 55, 739—742).—Two lactating goats maintained a positive calcium balance in five out of six periods investigated when fed on a ration consisting of grain, dry hay, and a starch paste in which calcium phosphate had been precipitated. Calcium assimilation was probably favoured by the fine state of division of the calcium phosphate. The magnesium balance was negative in each case. These results suggest that the different effects on the calcium balance of diets containing green and dry hay (Hart, Steenbock, and Hoppert, A., 1921, i, 829) is in part due to differences in the states of aggregation of the cell contents of the two feeding-stuffs. E. S.

**The Effect of Air which has been Exposed to the Radiations of the Mercury-vapour Quartz Lamp in Promoting the Growth of Rats, fed on a Diet Deficient in Fat-soluble Vitamins.** ELEANOR MARGARET HUME and HANNAH HENDERSON SMITH (*Biochem. J.*, 1923, 17, 364—372).—Rats fed on a diet deficient in fat-soluble vitamins showed a prolongation of normal growth when kept in glass jars which have been exposed to the mercury-vapour quartz lamp for ten minutes every second day. When the animals were kept in jars from which the irradiated air was displaced no prolongation of growth was observed. Evidence is produced that the ozone generated by the lamp is not responsible for this phenomenon. S. S. Z.

**The Action of Sodium Chloride on the Constituents of the Cell Nucleus.** MARIO GARCIA BANUŠ (*Z. physiol. Chem.*, 1923, 28, 135—140).—Treatment of cells with sodium chloride solution reduces the fraction of the nucleoprotein of which the protein can be extracted by acid. This is demonstrated directly, and also by a study of the staining properties of such cells. W. O. K.

**The Composition of Herring Ova. I. Ichthulin.** H. STEUDEL and E. TAKAHASHI (*Z. physiol. Chem.*, 1923, 127, 210—19).—Ichthulin obtained from herring ova by extraction first with sodium chloride solution and then with a dilute solution of sodium hydroxide yielded the following results on analysis: C, 52.3%; H, 7.6%; N, 14.1%; P, 0.014%; S, 0.895%; Fe, 0%. The presence of 1.28% of histidine, 6.33% of arginine, and 4.81% of lysine was shown by analysis by the method of Kossel and Jutscher. W. O. K.

**The Composition of Herring Ova. II. The Skin of the Ova.** H. STEUDEL and S. OSATO (*Z. physiol. Chem.*, 1923, 127, 20—223).—If the ova of the herring are extracted repeatedly with dilute alkali the skin is left. This has the following composition: C, 51.5%; H, 7.8%; N, 14.1%; P, 0.07%; S, 0.55%; histidine, 2.1%; arginine, 6.3%; lysine, 5.5%. The relation to ichthulin is very close, and it is suggested that the skins may be composed of an insoluble modification of ichthulin. W. O. K.

**Total Non-protein Nitrogen Content of the Hen's Egg.** S. HEPBURN (*J. Amer. Inst. Homeopathy*, 1922, 15, 409—412).—The protein-free filtrate, obtained by dilution of white, yolk, or whole egg with water and treatment with 10% sodium tungstate solution and 0.67*N*-sulphuric acid, may be used for the estimation of total non-protein nitrogen by Kjeldahl's method. From estimations made on thirty-six samples from various sources, the conclusion is drawn that the total non-protein nitrogen of white, yolk, and whole egg may vary within wide limits, and may not be taken as the sole criterion of edibility; some edible eggs showed a high value for total non-protein nitrogen, and some inedible eggs a low value for that constituent. Several % of the total nitrogen of fresh eggs may be present in the non-protein form.

#### CHEMICAL ABSTRACTS.

**Can the Animal Organism Synthesise Cholesterol?** S. J. HANNHAUSER and HANS SCHABER (*Z. physiol. Chem.*, 1923, 127, 78—280).—By comparison of the cholesterol content of incubated and unincubated eggs, it is shown that the total cholesterol content decreases by an average amount of about 11% in twenty-one days. The free cholesterol suffers a decrease of about 26%, whilst cholesterol esters increase 128%. Apparently no synthesis of cholesterol takes place during incubation. W. O. K.

**Decomposition of Arginine in the Liver.** K. FELIX and M. OMITA (*Z. physiol. Chem.*, 1923, 128, 40—52).—The liver of cats decomposes arginine into urea and ornithine. 90% of the theoretical quantity of urea may be obtained after perfusion of the

liver. The liver of geese, on the other hand, is without influence on arginine.

W. O. K.

**The Significance of the Kidney in the Synthesis of Hippuric Acid in Man, Dog, Pig, and Sheep.** I. SNAPPER, A. GRÜNEIR and J. NEUBERG (*N. T. v. Gen.*, 1923, 67, 1, 5, 426; from *Physiol. Abstr.*, 1923, 8, 107).—The surviving kidney of the dog, pig, sheep, or man was shown to be capable of forming hippuric acid from sodium benzoate and glycine, whereas after double nephrectomy the dog cannot synthesise hippuric acid. Synthesis and excretion of hippuric acids are separate functions. When the perfusion pressure is so low that no ureteral filtrate is formed there is still hippuric acid formation; the rate of formation of hippuric acid cannot therefore be used as a test of renal function in man. W. O. K.

**The Possible Significance of Hexosephosphoric Esters in Ossification.** ROBERT ROBISON (*Biochem. J.*, 1923, 17, 286–293).—An enzyme is established in the ossifying cartilage of young rats and rabbits which rapidly hydrolyses hexosemonophosphoric acid, yielding free phosphoric acid. Non-ossifying cartilage shows less than one-tenth of the hydrolytic power of ossifying cartilage. This hydrolytic action is also manifested by the kidney, but the activity is only about 50% of that of an equal weight of epiphyseal cartilage. Other tissues contain the enzyme in a very much lower degree, muscle and blood being almost inactive. Glycerophosphoric acid is hydrolysed by the same tissues in approximately the same order. One of the two phosphoric acid groups of hexosediphosphoric acid is very readily hydrolysed by almost all tissues, including muscle and non-ossifying cartilage, except blood. The possible significance of this enzyme in the process of ossification in the animal body is discussed.

S. S. Z.

**The Serum Proteins of Milk.** W. GRIMMER, C. KURTENACKER, and R. BERG (*Biochem. Z.*, 1923, 137, 465–483).—The serum proteins of milk are as a rule incompletely precipitated by heat, acids, or salts. Calcium chloride is used on the large scale for coagulating the protein of whey. The residual nitrogen content of serum after precipitation of proteins by phosphotungstic acid is 0.027% or after tannin 0.028%. This proportion is sensibly constant and is unaffected by heating the milk or the serum. Heating serum lessens the digestibility of the proteins and rennin-whey protein is more difficultly digestible than casein. Brief action of rennin produces a greater proportion of heat-coagulable protein than is found after protracted action of rennin. In the latter case, products are formed which are not heat-coagulable. The tryptophan content of milk-serum lies between 0.012 and 0.021%. The heat-coagulable proteins and uncoagulable protein have the same tryptophan content, 3.1%. In the mother-liquor, tryptophan is not detectable.

H. K.

**Sugar Elimination after the Subcutaneous Injection of Dextrose in the Dog.** STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1923, 55, 769–794).—Experiments have been

made on the tolerance of the dog for dextrose when injected simultaneously immediately after a meal. Following doses of 0.4 g. per kg. of body-weight, there was an increased excretion of "total" sugar, but not of fermentable sugar or of di- or poly-saccharides, which persisted during the greater part of the day of the experiment; with doses of 4 g. per kg., the urinary sugar remained above the normal for more than twenty-four hours; with still larger doses (6, 7, and 8 g. per kg.) there was an increased excretion, extending into the second day after the injection, of all forms of sugar in the urine. In one experiment, the content of sugar in the urine, following the injection of 7 g. per kg. of body-weight, was 1.21% at a time when that of the blood was only 0.12%. This is interpreted as indicating that the sugar excreted in the urine does not represent the diffusion through the kidney of an excess of dextrose, but is due rather to the excretion of some waste sugar, possibly one of the isomeric  $\alpha$ - and  $\beta$ -glucoses, which is not readily utilised by the organism. The lag in the excretion of sugar can also be explained on the same lines.

The greater part of the paper is devoted to a criticism of a recent publication of Folin and Berglund (A., 1922, i, 487). It is pointed out that, with the excessive doses (200 g.) of sugar employed by these authors, the absorptive and eliminative processes would not be normal, and hence the results from their experiments are not comparable with those obtained by others (cf., for example, A., 1918, i, 322) using smaller amounts of sugar. Further, the postulation of an "emotional hyperglycæmia," due to the pain produced by drawing blood, is considered unwarranted (cf. Foster, *loc. cit.*, vol. i, 503). But the main criticism is directed towards the interpretation of the results, some of which are discussed in detail. It is maintained that Folin and Berglund have consistently misinterpreted their results, which, so far from supporting the conception of a definite glucose threshold for normal human beings, are in agreement with the view that the organism has no absolute tolerance for sugar during digestion. The criticism is extended to many other points.

E. S.

**Rate of Excretion of Urea. VII. Effect of Various Other Factors than Blood Urea Concentration on the Rate of Excretion of Urea. VIII. Effect of Changes in Urine Volume on the Rate of Excretion of Urea.** T. ADDIS and D. R. DRURY *J. Biol. Chem.*, 1923, 55, 629—638, 639—651).—VII. Increased rates of excretion of urea are produced by the ingestion of milk, caffeine, or glutamic acid, and decreased rates by exercise or by the injection of pituitrin or of large amounts of adrenaline. At the same time, the proportionality between the rate of excretion of urea and its concentration in the blood (this vol., i, 511) is disturbed, thus indicating that the above changes take place independently of changes in the concentration of urea in the blood. VIII. Under otherwise constant conditions, the rate of excretion of urea is not influenced by changes in the volume of the urine.

E. S.

**Creatinine Excretion in Urine. Criticism of Ambard's Theory.** WILHELM LAUFBERGER (*Biochem. Z.*, 1923, 137, 531-535).—Ambard's theory is shown experimentally to be untenable, and so likewise any amplification or extension of it. H. K.

**Effect of some Organic Acids on the Uric Acid Excretion of Man.** H. V. GIBSON and EDWARD A. DOISY (*J. Biol. Chem.*, 1923, 55, 605-610).—Ingestion of the sodium salt of pyruvic acid produced an increased excretion of uric acid. Sodium lactate, on the other hand, caused a decreased excretion. The latter effect was probably due to an increased threshold of the kidney for uric acid, since a slight rise in the uric acid content of the plasma was observed (cf. Lewis, Dunn, and Doisy, A., 1918, i, 277). E. S.

**The Purine Bases in the Urine on a Diet Poor in Purines. (The Question of the Origin and Treatment of Gout.)** H. STEUDEL and J. ELLINGHAUS (*Z. physiol. Chem.*, 1923, 127, 291-298).—The purine bases in the combined urines of two persons on diets poor in purines were found to consist of 71 mg. sodium heteroxanthine, 43 mg. of paraxanthine, and 56 mg. of methylxanthine (from 23.6 litres of urine).

The metabolism of nucleic acids depends very much on the bacterial decompositions proceeding in the intestines (cf. this vol., i, 270). This is of importance in connexion with gout. W. O. K.

**The Porphyrin of Human Fæces.** A. PAPENDIECK (*Z. physiol. Chem.*, 1923, 128, 109-118).—The porphyrin excreted in the fæces appears to depend on the diet and to be largely exogenous in nature. Chiefly from a study of the adsorption spectra, it is concluded that the porphyrin in the fæces is not a single individual, and that it is not the same as the porphyrin of urine.

W. O. K.

**Cholesterol in Beri-Beri in Pigeons. II.** KAZUO HOTTA (*Z. physiol. Chem.*, 1923, 128, 85-99; cf. this vol., i, 512).—The blood, stomach, and brains of pigeons suffering from avian beri-beri show very early an increase of cholesterol as compared with those from normal animals. Breast-muscles, spleen, heart, liver, and pancreas show increases only in the later stages of the disease. The kidney and testicles do not show any increase. W. O. K.

**The Balance of Anions and Cations in the Plasma in Nephritis.** JOHN MARRACK (*Biochem. J.*, 1923, 17, 240-259).— $[\text{HPO}_4]'$ -ions were found to be increased in the majority of cases with high blood urea, whilst no increase was observed in sodium-ions. A very low figure for chlorine-ions in plasma was recorded in severe cases of nephritis. Evidence of a disturbance in the distribution of chlorine-ions between the plasma, on the one hand, and cerebrospinal fluid and tissues, on the other, is produced. The excess of cations in normal plasma unaccounted for by  $[\text{HCO}_3]$ ,  $\text{Cl}'$ , and  $[\text{HPO}_4]'$  is combined mainly with protein. In many cases of nephritis with much urea retention, an excess of cations over the above combinations has been established. These were

combined with undetermined anions. In most cases of acidosis in nephritis the reduction of plasma  $[\text{HCO}_3]'$  was due to accumulated  $[\text{HPO}_4]'$ -ions and undetermined anions. The  $[\text{HCO}_3]'$  of cerebrospinal fluid is the same as that of the plasma. Reduction of  $[\text{HCO}_3]'$  in cerebrospinal fluid is caused by excess of chlorine-ions.  
S. S. Z.

**Inorganic Salt Metabolism. II. Inorganic-ion Ratio after Administration of Oxalates and Citrates.** E. G. GROSS (*J. Biol. Chem.*, 1923, 55, 729—738; cf. A., 1922, i, 1210).—The subcutaneous injection of sodium oxalate produces tetany in dogs. At the same time there is a decrease in the sodium, chlorine, and calcium, and an increase in the potassium and total phosphorus content of the blood; that of magnesium, however, remains constant. Sodium and chlorine decrease in approximately the same proportion; a similar relation holds for the increase in potassium and phosphorus. Neither tetany nor a disturbance in the salt-content of the blood is produced by injection of sodium citrate.  
E. S.

**The Influence of Benzene on certain Aspects of Metabolism.** F. P. UNDERHILL and B. R. HARRIS (*J. Ind. Hyg.*, 1923, 4, 491—500).—Benzene not only acts on the blood elements but also exerts a catabolic influence on body-tissues as a whole, as manifested by a sharp rise in creatinine and total nitrogen, within a very short period after its subcutaneous injections into rabbits, far in excess of that found in rabbits under similar conditions under ordinary starvation.  
CHEMICAL ABSTRACTS.

**Action of Cyanamide. III. Quantitative Estimation of Cyanamide in the Cell.** H. RAIDA (*Zeit. ges. exp. Med.*, 1923, 31, 215—220; from *Physiol. Abstr.*, 1923, 8, 107).—Cyanamide is converted into urea in the body. Sub-lethal doses of cyanamide have the capacity to promote oxidation of sugar in the animal body. Pulp of liver only has the capacity of converting cyanamide into urea. The conversion of cyanamide could not be produced in vitro by any means.  
W. O. K.

**Can Fasting Fowls Synthesise Glycine or Ornithine?** J. G. M. BULLOWA and C. P. SHERWIN (*Proc. Soc. Exp. Biol. Med.*, 1922, 20, 125—128; from *Physiol. Abstr.*, 1923, 8, 107).—Starving hens furnish a very small amount of ornithine when this is necessary for the detoxication of benzoic acid. No hippuric acid was found in the urine of well-fed birds after feeding with benzoic acid but only benzoyl-ornithine or free benzoic acid. Birds are unable to furnish glycine for detoxication purposes, and even unable to make use of it, if it is supplied to them from exogenous sources.  
W. O. K.

**Pharmacology of some Phenylenediamines.** P. J. HANZLIK (*J. Ind. Hygiene*, 1923, 4, 386—409, 448—462).—The pharmacology of *m*- and *p*-phenylenediamines and their dimethyl and diethyl derivatives is studied. Because of their lipid solubility, these compounds may be absorbed through the skin to give toxic effects.

Stimulation of circulation, and respiration, fall of body temperature, tremors, convulsions, coma, and death follow the subcutaneous injection of the compounds into mammals. The injection of *p*-phenylenediamine into rabbits produces a characteristic oedema of the face, tongue, and nose.

CHEMICAL ABSTRACTS.

**Poisoning by Pure Methyl Alcohol.** G. REIF (*Z. angew. Chem.*, 1923, 36, 276).—It had been previously stated by Theiler (*ibid.*, 148) that poisoning by methyl alcohol is due to the presence of impurities. More recently, however, the consumption of methyl alcohol, subsequently found to be chemically pure, has proved fatal in several cases.

J. B. F.

**Rate of Liberation of Acid by  $\beta\beta'$ -Dichlorodiethyl Sulphide and its Analogues in its Relation to the "Acid." Theory of Skin Vesication.** RUDOLPH ALBERT PETERS and ERNEST WALKER (*Biochem. J.*, 1923, 17, 260—276).—The theory that the intracellular liberation of acid is responsible for the vesicant action of dichlorodiethyl sulphide is not supported by experimental evidence, as the vesicant action and the rate of acid liberation do not run parallel. Thus the comparative rates of acid liberation in a 5% alcoholic solution were found to be as follows:  $\beta\beta'$ -Dichlorodiethyl sulphide, 100 (vesicant);  $\alpha\alpha'$ -dichlorodimethyl sulphide, 500 (non-vesicant);  $\alpha\beta\beta'$ -trichlorodiethyl sulphide, nil (non-vesicant);  $\alpha\beta\beta\beta'$ -tetrachlorodiethyl sulphide, 4 (non-vesicant);  $\alpha\alpha\beta\beta\beta\beta'$ -hexachlorodiethyl sulphide, 1 (non-vesicant);  $\beta\beta'$ -dichlorodiethylsulphone, 1 (vesicant). In the case of  $\beta\beta'$ -dichlorodiethyl sulphide, the liberation of acid at constant temperature is decreased by increasing concentrations of alcohol and sodium chloride. The presence of sodium chloride does not inhibit the liberation of acid in dichlorodimethyl sulphide. One % sodium nitrate does not influence the rate of acid liberation by dichlorodiethyl sulphide. Sodium sulphate and magnesium sulphate inhibit the rate strongly in the later stages of the reaction. The velocity constant of the reaction calculated from the unimolecular formula showed a steady, small rise from 30—80% hydrolysis, and this rise was influenced by different experimental conditions, from which the authors conclude that the reaction is a two-stage reaction. Between 15° and 38°, the temperature coefficient of the reaction is 3.3 per 10° rise in temperature.

S. S. Z.

## Chemistry of Vegetable Physiology and Agriculture

**Certain Phases of Nitrogenous Metabolism in Bacterial Cultures.** G. C. DE BORD (*J. Bact.*, 1923, 8, 7—45).—The presence of dextrose in peptone media increases the rate of production of amino-nitrogen in growing cultures of *Bacillus coli*, *Ps. pyocyanea*, *B. subtilis*, *C. botulinum*, and *C. sporogenes*. The amino-nitrogen in bacterial cultures is an approximate index

under certain conditions of proteolysis. Folin's method for the estimation of amino-nitrogen is applicable to peptone media. The ammonia found in bacterial cultures is not a trustworthy index of bacterial proteolysis. The presence of fermentable carbohydrate in bacterial cultures affects the nitrogenous metabolism. Some bacteria destroy dextrose without a marked increase in hydrogen-ion concentration. Hence the  $p_H$  is not an index of the destruction of dextrose.

CHEMICAL ABSTRACTS.

**The Effect of Small and of Large Quantities of Humus on the Fixation of Nitrogen by *Azotobacter chroococcum*.** J. MOUQUET (*Compt. rend.*, 1923, 176, 1421—1423).—The author has studied the fixation of nitrogen both absolutely and relatively to the amount of sugar consumed. For the smaller quantities of humus, the amount of nitrogen fixed increases approximately in proportion, the ratio of nitrogen fixed to sugar consumed remaining constant. For the larger additions of humus, the amount of nitrogen fixed increases but at a smaller rate; the nitrogen-sugar ratio, however, shows a very marked increase. The suggestion is made that a substance, present in traces only, intensifies the fixation without increasing the yield whilst in larger amounts it increases both intensity of fixation and yield (cf. Bertrand, A., 1912, ii, 377).

H. J. E.

**Oxidation of Selenium by a New Group of Autotrophic Micro-organisms.** JACOB G. LIPMAN and SELMAN A. WAKSMAN (*Science*, 1923, 57, 60).—In addition to *Thiobacillus thio-oxidans* (cf. A., 1922, i, 303), a group of bacteria able to derive their energy from the oxidation of selenium to selenic acid must also be classified among the strictly (obligate) autotrophic bacteria.

A. A. E.

**The Viscosin of Fungi.** NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 37, 320—330).—The unripe fruits of *Lycoperdon piriforme* contain between 11 and 25.8% of the mucin, viscosin. This contains 6.1—5% of nitrogen and 0.98—1.14% of phosphorus, and after hydrolysis 92% of the total nitrogen is present as amino-groups. The main products of hydrolysis are glucosamine and phosphoric acid. In ripe fruits, substances of the chitosan type were isolated containing 5.37—6.7% of nitrogen and 0.9—3.9% of phosphorus, and adding glucosamine on hydrolysis.

H. K.

**The Nature of the Protein of Fungi.** NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 137, 331—340).—By hydrolysis of the powder of the ripe fruits of *Lycoperdon piriforme* by means of 2% sulphuric acid, pepsin, or brief warming with concentrated hydrochloric acid, two substances were isolated: (1) a peptone-like substance with 16.6% of nitrogen, soluble in 80% alcohol, and on complete hydrolysis yielding 58% of nitrogen precipitable by phosphotungstic acid. (2) An alcohol insoluble substance—a chitosan containing 4% of nitrogen and a variable content of phosphorus. On hydrolysis, it gave glucosamine. On one occasion, the parent protein of the fungus was isolated and on partial hydrolysis it gave the two fragments mentioned.

H. K.

**The Fermentation of Dextrose and Lævulose by Dried Yeast in the Simultaneous Presence of Phosphate and Sulphite.** FUMIWO HEMMI (*Biochem. J.*, 1923, 17, 327—333).—Acetaldehyde is produced to about the same extent when dextrose and lævulose are fermented by dried yeast in the presence of phosphate. The acetaldehyde formed in the process of fermentation was fixed by sodium sulphite. The fermentation of potassium hexosephosphate also yields acetaldehyde in the presence of sodium sulphite.

S. S. Z.

**The Specific Action of Carbohydrates on Embryos.** F. BOAS and F. MERKENSCHLAGER (*Biochem. Z.*, 1923, 137, 300—311).—In presence of galactose in preference to any other carbohydrate examined, calcium nitrate and chloride, although inimical to the growth and sprouting of lupin seeds, are tolerated. Seeds containing little fats are more sensitive to calcium-ions than seeds rich in fats. Unexpectedly, digitonin stimulated sprouting.

H. K.

**The Glycerylphosphatase of Plant Seeds.** I. ANTONIE NÈMEC (*Biochem. Z.*, 1923, 137, 570—575).—The properties of the glycerylphosphatase of various seeds have been studied in relation to the substrate sodium glycerylphosphate. The course of the reaction follows Schütz's rule, the amount of glycerylphosphate decomposed being proportional to the square root of the time. A state of equilibrium is finally attained. As the quantity of enzyme is increased, the amount of hydrolysis is not proportional, but somewhat less. The amount of phosphate set free by autolysis is, however, proportional to the amount of enzyme used. With increasing initial amounts of glycerylphosphate, the amount of enzymatic hydrolysis is proportional to the square root of the original glycerylphosphate concentration, if the concentration be between 0.05 and 1%. Glycerol has an inhibiting influence in concentrations above 5%. The optimum temperature for glycerylphosphatase action is 35°, the amount of hydrolysis being proportional to the square root of the temperature. The seeds used were yellow and white mustard seeds and soja beans.

H. K.

**The Investigation of Humic and Fatty Matter in Soil by means of Pyridine.** MAURICE PIETTRE (*Compt. rend.*, 1923, 176, 1329—1331).—A mixture of equal proportions of pyridine and water is the most suitable solvent for the extraction of humus from soils. Free humus is extracted directly; combined humus from the residue after acidification with hydrochloric acid. Alternatively, total and free humus may be investigated, the proportion combined being found by difference. Pyridine also extracts other substances of a fatty nature from the soil, and methods are indicated for the separation of such substances from the dry pyridine extract.

H. J. E.

## Organic Chemistry.

**A Method for the Naming of All Organic Compounds.** I. SHERLOCK WHEELER (*Chem. News*, 1923, 126, 113—115).—A system of nomenclature based on the author's linear system of representing the structure of organic compounds (cf. this vol., 173). The original must be consulted, as the paper does not end itself to abstraction.

**The Foundation of an Electronic Theory of Organic Compounds.** A. L. MARKMAN (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 44—153).—Berkenheim's theory (this vol., i, 525) is adversely criticised; it is regarded as useless even as a working hypothesis.

R. T.

**Petroleum.** W. RAMSAY (*J. Soc. Chem. Ind.*, 1923, 42, 287—288r).—A large number of samples of mineral oils and asphalts from different parts of the world are found to contain nickel, held in solution or colloidal suspension, in amounts varying from 1 to more than 200 parts per million. This observation lends support to the theory of Sabatier and Senderens that petroleum is formed by catalytic hydrogenation of natural gas.

E. H. R.

**Reduction of Carbon Monoxide to Methane in Presence of Iron under Increased Pressures.** F. FISCHER and H. TROPSCH (*Brennstoff-Chem.*, 1923, 4, 193—197; cf. following abstract).—In contact with iron filings at a temperature of about 400°, carbon monoxide is reduced to methane, but only in small amounts unless the pressure be increased to about 40 atmospheres. Freshly used iron does not catalyse the reaction; the metal must be in contact with the gases for some time before it becomes activated. Once formed, however, the catalyst retains its activity in presence of pure gases for a considerable time, but a gas contaminated with sulphur compounds rapidly renders it useless. With time, the filings gradually lose their structure and form a powder of iron, iron carbide, and carbon—the carbon is produced from the carbon monoxide with simultaneous formation of carbon dioxide. The main reaction occurring is the formation of carbon dioxide and methane in equal volumes from two volumes of carbon monoxide and two of hydrogen. The best result obtained was from a gas containing 40% of carbon monoxide and 50% of hydrogen at 20° and 40 atmospheres; there was 33.5% of methane in the issuing gas. A certain amount of ethane was also produced.

T. S. W.

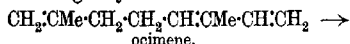
**Reduction of Carbon Monoxide to Methane in Presence of Iron at Ordinary Pressures.** F. FISCHER, H. TROPSCH, and V. MOHR (*Brennstoff-Chem.*, 1923, 4, 197; cf. preceding abstract).—At 400°, little methane is produced from a mixture of carbon vol. CXXIV. i.

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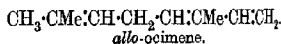
monoxide and hydrogen in contact with iron at the ordinary pressure. Even a catalyst which had been activated by the formation of iron carbide by exposure to a mixture of carbon monoxide and hydrogen at increased pressures gave a gas containing only 1.9% of methane from an approximately equimolecular mixture of the gases under test. The main reaction is formation of carbon and carbon dioxide.

T. S. W.

**$\Delta^7$ -Heptatriene and certain Related Substances.** C. J. ENKLAAR (*Rec. trav. chim.*, 1923, 42, 524—527).—The paper deals chiefly with the question of the structure of  $\Delta^7$ -heptatriene, previously obtained by heating  $\alpha$ -heptadiene-6-ol with potassium hydrogen sulphate (A., 1913, i, 244, 330), based on an investigation of its optical properties. The refraction and dispersion were found to be abnormal, which was attributed, in part, to polymerisation. Some of the hydrocarbon was fractionated from sodium; the middle portion boiling at 110—112° at 758 mm., had  $d_4^{20}$  0.755 and its analysis agreed with the formula  $C_7H_{10}$ . After keeping in a sealed tube for three weeks, it had  $d_4^{20}$  0.7577, and after three months it had risen to  $d_4^{20}$  0.765 so that some polymerisation must have occurred, but this would not account fully for the optical abnormalities exhibited. The author therefore suggests that heptatriene (and hexatriene) prepared by the use of potassium hydrogen sulphate may be stereoisomeric forms stable to acids, whilst the hexatriene obtained from the corresponding bromide by means of zinc represents the corresponding unstable stereoisomeride. It is also suggested that *allo*-ocimene has not the formula  $CH_2:CH:CH:CH:CMc:CHMe$  but is formed from ocimene in the following way:



ocimene.

*allo*-ocimene.

F. A. M.

**The Order of Elimination of Hydrogen Halides from Mixed Halogen Derivatives of Saturated Open-chain and Cyclic Hydrocarbons from the Stereochemical Point of View.** AL. FAVORSKI and TATIANA FAVORSKAÏA (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 304—311).—It has been shown by Favorski and Boshovsky (A., 1912, i, 616) that when 1-chloro-1:2-dibromocyclohexane was treated with an alkali hydroxide, hydrogen chloride and not hydrogen bromide was eliminated, the resulting compound being 1:2-dibromo- $\Delta^1$ -cyclohexene. The reactions leading to the formation of this substance have now been repeated, using diethyl ketone in the place of cyclohexanone as starting material.

Diethyl ketone was converted by the action of phosphorus pentachloride followed by alcoholic potassium hydroxide into  $\gamma$ -chloro- $\Delta^6$ -pentene,  $CHMc:CEtCl$ , b. p. 90—92°/781 mm.,  $d_4^{20}$  0.9305,  $d_4^{25}$  0.9125,  $[R_D]_D$  29.66. The action of bromine in chloroform led to  $\gamma$ -chloro- $\beta$ - $\gamma$ -dibromopentane,  $CHMcBr:CEtClBr$ , b. p. 83—85°/14

nm.,  $d_4^{20}$  1.8222,  $d_4^{25}$  1.7940, which, on treatment with alcoholic sodium ethoxide, loses hydrogen bromide and passes into  $\gamma$ -chloro-3-bromo- $\Delta^2$ -pentene, b. p. 40—42°/8 mm.,  $d_4^{25}$  1.4730,  $[R_L]_D^{25}$  36.88.

The reason for the difference in the behaviour of the open-chain and the cyclic compound is explained by the fact that in the latter the configuration of the chlorodibromo-compound is such that hydrogen and chlorine are in a *cis*-position to one another, making the elimination of hydrogen bromide impossible, whilst in the open-chain there is free rotation about the two carbon atoms carrying the halogen atoms and the elimination of hydrogen halide can proceed normally.

G. A. R. K.

**Chloromethanesulphonic Acid.** RENÉ DEMARS (*Bull. Sci. Pharmacol.*, 1922, 29, 425—431; from *Chem. Zentr.*, 1923, i, 500).—Chloromethanesulphonic acid may be prepared by the action of sodium sulphite on chlorobromomethane,  $\text{CH}_2\text{ClBr} + \text{Na}_2\text{SO}_3 = \text{NaBr} + \text{CH}_2\text{Cl}\cdot\text{SO}_3\text{Na}$ , or by oxidation of chloromethyl thiocyanate with nitric acid and separation by way of the barium salt.

G. W. R.

**Preparation of Alcohols and Aldehydes.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 362537; Swiss Pats. 94603 and 95456; Brit. Pat. 175238; from *Chem. Zentr.*, 1923, ii, 473—479).—A modification of earlier patents (D.R.-P. 350048; Swiss Pat. 93277; Brit. Pat. 158906), whereby for the catalytic reduction of acetaldehyde or other aldehydes, a copper catalyst is prepared either by mixing powdered copper and water glass or colloidal silicic acid with pumice, oxidising at 200°, and then reducing at 250°, or by mixing copper formate with pumice and reducing at 200—250°, or by reducing malachite at 200—250°. Other activators may be used in place of water glass or colloidal silicic acid. Ethyl alcohol is prepared by passing acetaldehyde or paracetaldehyde vapour mixed with hydrogen over the catalysts thus prepared, at about 60°. In a similar way, methyl alcohol and benzyl alcohol are prepared from the corresponding aldehydes.

G. W. R.

**Tertiary Methylheptenols. I. Their Ketonic Decomposition.** VICTOR GRIGNARD and R. ESCOURROU (*Compt. rend.*, 1923, 176, 1860—1863).—A study of the effect of heat, etc., on various substituted methylheptenols, including the *isopropyl*, *ethyl*, and *isoamyl* derivatives. These were prepared by Grignard's method from three different samples of methylheptenone, as obtained (1) from citral, (2) from lemon-grass oil, and (3) from the residues of the manufacture of  $\psi$ -ionone. All three products consist of the  $\alpha$ -form,  $\text{CH}_3\cdot\text{CMe}\cdot(\text{CH}_2)_3\cdot\text{COMe}$ , and (in larger proportion) the  $\beta$ -form,  $\text{CMe}_2\cdot\text{CH}\cdot(\text{CH}_2)_3\cdot\text{COMe}$ . In the preparation of a heptenol, the latter substance (two mols.) undergoes condensation to give the compound  $\text{CMe}_2\cdot\text{CH}\cdot(\text{CH}_2)_3\cdot\text{CMe}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}_2$ . The lower members of the above heptenol series do not readily pass into -dienes except in presence of energetic dehydrating agents, of which the best is metaphosphoric acid, used in large excess to prevent the formation of the pyro-acid, which induces cyclisation.

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Anhydrous oxalic acid, at 150°, produces simultaneous dehydration and cyclisation to give *cyclogeraniolenes*, except in the case of phenylmethylheptenol, which is dehydrated even if distilled under diminished pressure, in presence of a trace of acid. Benzylmethylheptenol is much less readily dehydrated. In the case of the alkyl derivatives, tendency to lose the elements of water increases with molecular weight. Thus, the preparation, by heating with acetic anhydride, of the acetyl derivatives of the higher members is rendered difficult owing to dehydration and ketonic decomposition. The latter (cf. Mme Ramart-Lucas, A., 1913, i, 1325) consists in the elimination of hydrocarbon:  $\text{CMe}_2\text{CH}(\text{CH}_2)_n\text{CMeR}\cdot\text{OH} \rightarrow \text{CMe}_2\text{CH}(\text{CH}_2)_n\text{COMe} + \text{R}\cdot\text{H}$ , and first becomes noticeable in the case of the propyl derivative ( $\text{R}=\text{Pr}^n$ ), which undergoes this decomposition on distilling under the ordinary pressure. The isopropyl derivative decomposes in this manner to the extent of 75%, even on distilling under 12 mm. pressure.

Phenylmethylheptenol undergoes no ketonic decomposition, but benzylmethylheptenol, on distilling under the ordinary pressure, is converted largely into methylheptenone and toluene. These ketonic decompositions are catalysed by traces of sulphuric acid and by colloidal platinum (e.g., in attempts at catalytic hydrogenation).  
E. E. T.

**Tertiary Methylheptenols. II. Their Catalytic Hydrogenation.** V. GRIGNARD and R. ESCOURBOU (*Compt. rend.*, 1923, 177, 93—96; cf. preceding abstract).—A further study of the substituted methylheptenols. Whilst the methyl and ethyl derivatives are readily reduced to the corresponding heptanols, the propyl and higher derivatives undergo ketonic decomposition. This produces the same experimental effect as a catalyst poison, so that either methylheptenone or its reduction product,  $\beta$ -methylheptan- $\zeta$ -ol may result (cf. Locquin and Wouseng, A., 1922, i, 710).

Dimethylheptenol, on reduction with hydrogen, in presence of nickel, gives  $\beta\zeta$ -dimethylheptane (reduction preceded by dehydration). When the reduction is carried out under diminished pressure, hydrogenation begins at 90°/15 mm., and is very vigorous at 90—100° in the case of the methyl, ethyl, and propyl derivatives. Normal reduction takes place without dehydration even at 160—170° when a pressure of 14 mm. is used. Thus at 160—170°/14 mm., dimethylheptenol is reduced quantitatively to  $\beta\zeta$ -dimethylheptan- $\zeta$ -ol. Methylpropylheptenol is quantitatively and normally reduced at 100°/15 mm. No ketonic decomposition occurs, nor is the speed of hydrogenation decreased by the use of low pressures. This fact is explained by assuming that, whereas, at the ordinary pressure, the adsorbed alcohol hinders renewed adsorption of hydrogen by the nickel catalyst, at low pressures only hydrogen is adsorbed.

The ease with which the alcohols in question are dehydrated appears to be due to the presence of the ethylenic linking, since the corresponding saturated alcohols, under similar conditions, do not undergo dehydration. The saturated alcohols obtained in the present work are colourless liquids, with b. p. density, and

refractive indices slightly lower than those of the corresponding unsaturated alcohols. They are readily dehydrated if heated with metaphosphoric acid.

The following constants were obtained: Substituted methylheptenols,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CH}_3$ . R=Me, b. p. 77—78°/13 mm., 173—175°/740 mm.,  $d^{20}_D$  0.8564,  $n^{20}_D$  1.45197. R=Et, b. p. 92.5—93°/13 mm., 197°/736 mm.,  $d^{20}_D$  0.8572,  $n^{20}_D$  1.45658. R=Pr, b. p. 102—103°/13 mm.,  $d^{20}_D$  0.8592,  $n^{20}_D$  1.45727. R=Pr<sup>i</sup>, b. p. 97—98°/12 mm.,  $d^{20}_D$  0.8717,  $n^{20}_D$  1.46295. R=n-butyl, 95—96°/5 mm., 119°/12 mm.,  $d^{20}_D$  0.8603,  $n^{20}_D$  1.45997. R=isoamyl, b. p. 123—124°/14 mm.,  $d^{20}_D$  0.8566,  $n^{20}_D$  1.45657. R=Ph, b. p. 144—145°/11 mm.,  $d^{20}_D$  0.9679,  $n^{20}_D$  1.52316. R=benzyl, b. p. 153—154°/10 mm.,  $d^{20}_D$  0.9654,  $n^{20}_D$  1.52632.

Substituted methylheptanols,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CH}_3$ . R=Me, b. p. 170—172°/760 mm.,  $d^{20}_D$  0.8162,  $n^{20}_D$  1.42831. R=Et, b. p. 84—85°/10 mm.,  $d^{20}_D$  0.8374,  $n^{20}_D$  1.43773. R=Pr, b. p. 105—106°/16 mm., 206—208°/741 mm.,  $d^{20}_D$  0.8458,  $n^{20}_D$  1.44917. R=n-butyl, b. p. 115°/14 mm.,  $d^{20}_D$  0.8526,  $n^{20}_D$  1.45537. R=isoamyl, b. p. 131—132°/20 mm.,  $d^{20}_D$  0.8444,  $n^{20}_D$  1.45007. R=benzyl, 155—156°/12 mm.,  $d^{20}_D$  0.9420,  $n^{20}_D$  1.50389. E. E. T.

### Alkylglycerols. I. Preparation of Alkylvinylcarbinols.

RAYMOND DELABY (*Bull. Soc. chim.*, 1923, [iv], 33, 602—626).—The synthesis of alkylglycerols from acetaldehyde, by conversion of the latter into alkylvinylcarbinols of the general formula  $\text{CH}_2\text{CH}_2\text{CHR}\cdot\text{OH}$  by means of the Grignard reagents, and subsequent bromination of the vinyl compounds, and replacement of bromine by hydroxyl, is contemplated, and the first stage of the synthesis involving the preparation of the alkylvinylcarbinols is now described. In practice, the best results were obtained by the interaction of equimolecular proportions of acetaldehyde and a magnesium alkyl bromide in ethereal solution at a low temperature, decomposition of the product with the theoretical amount of ice and acid, and rectification of the carbinol in a vacuum. The yields with the lower members ranged from about 30—50%. With the higher members, e.g., nonylvinylcarbinol, only traces were obtained. The following constants are given. Methylvinylcarbinol, b. p. 94—96°,  $d^{20}_D$  0.854,  $n^{20}_D$  1.4087. Ethylvinylcarbinol, b. p. 17°/20 mm.,  $d^{20}_D$  0.856,  $n^{20}_D$  1.4182. Propylvinylcarbinol, b. p. 33.5—34°,  $d^{20}_D$  0.851,  $n^{20}_D$  1.4215. n-Butylvinylcarbinol, b. p. 53.5—54°,  $d^{20}_D$  0.852,  $n^{20}_D$  1.4275. Nonylvinylcarbinol, b. p. about 12°/9 mm. In the preparation of all these substances considerable quantities of high boiling fractions were invariably obtained. These fractions were fully investigated both by chemical methods including oxidation, acetylation, benzoylation, etc., and also by microscopic methods, but no decisive results were obtained. A complicated mixture was apparently in question in every case, the constituent of which was possibly a polymeride of the alkylvinylcarbinol. As the phenylurethanes of these alkylvinylcarbinols were liquid substances, the allophanates were prepared for purposes of characterisation by leading cyanic acid vapours into the carbinol

and crystallising the products from alcohol. The allophanic ester of methylvinylcarbinol,  $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CH}_2\text{CH}_3$ , forms needles, m. p.  $151\text{--}152^\circ$ , and the corresponding derivative of ethylvinylcarbinol had m. p.  $152\text{--}153^\circ$ , of propylvinylcarbinol, m. p.  $139\cdot5\text{--}140^\circ$ , and of butylvinylcarbinol, m. p.  $156\cdot5\text{--}157^\circ$ . The phenylurethane of butylvinylcarbinol was a liquid, b. p.  $200\text{--}202^\circ/24\text{ mm.}$  Experiments on the resolution of butylvinylcarbinol into its optical enantiomorphs are described, involving the crystallisation of the strychnine salt of the acid phthalic ester from acetone. The least soluble salt gave on subsequent hydrolysis *l*-butylvinylcarbinol, having  $\alpha_D -23\cdot3^\circ$ . The *d*-isomeride was not isolated in a pure condition.

G. F. M.

**Preparation of Methyl and Ethyl Ethers.** J. B. SENDERENS (*Compt. rend.*, 1923, 177, 15—19; cf. this vol., i, 432).—The usual assumption that the equations: (a)  $\text{EtOH} + \text{H}_2\text{SO}_4 = \text{EtHSO}_4 + \text{H}_2\text{O}$ , (b)  $\text{EtHSO}_4 + \text{EtOH} = \text{H}_2\text{SO}_4 + \text{Et}_2\text{O}$ , represent fully the etherification process is incorrect. Evidently, not  $\text{H}_2\text{SO}_4$ , but  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$  is produced in (b), and, as the reaction proceeds, higher hydrates still, depending on the temperature used. When the hydrate,  $\text{H}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ , is heated, boiling commences at  $121^\circ$ . The rise of temperature from  $121\text{--}127^\circ$  corresponds with the formation of  $\text{H}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$ , that from  $127\text{--}135^\circ$  to  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ , that from  $135\text{--}148^\circ$  to  $\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$ , and that from  $148\text{--}170^\circ$  to  $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ . In presence of alcohol, the penta-, tetra-, tri-, and di-hydrates correspond with the (different) ranges:  $110\text{--}121^\circ$ ,  $121\text{--}130^\circ$ ,  $130\text{--}145^\circ$ , and  $145\text{--}162^\circ$ , respectively. At a temperature as low as  $145^\circ$ , ethylene tends to be formed to the exclusion of ethyl ether. Its formation begins actually at  $140^\circ$ , and is accelerated by the impurities which accumulate in the reaction mixture. No ethylene is formed at  $130^\circ$ , the temperature favoured by many ether manufacturers, but the effective hydrate is here the tetra-hydrate, which has poor etherifying properties.

At  $136\text{--}138^\circ$ , whilst very little ethylene is formed, etherification is more rapid than at  $130^\circ$ , the trihydrate being stable at this temperature.

It is better to supply a continuous ether-still with 95% alcohol containing 10% of concentrated sulphuric acid ( $d\ 1\cdot842$ ) than to supply alcohol alone. On the other hand, addition of alcohol containing acid corresponding with  $\text{H}_2\text{SO}_4\cdot 2\cdot5\text{H}_2\text{O}$  has no beneficial effect.

The conversion of methyl alcohol into methyl ether is not complicated by the possibility of ethylene formation, and accordingly the ether can be prepared at such a temperature that the effective hydrate is  $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ , which is a great advantage. Thus at  $160\text{--}165^\circ$ , using quantities of 100 c.c. of methyl alcohol, in a continuous process, methyl ether was formed at the rate of 250—300 c.c. per minute (the tri- and tetra-hydrates giving, at  $130^\circ$ , respectively, 120 and 24 c.c. per minute).

E. E. T.

**Hydrolysis of the Sulphoxide and the Sulphone of  $\beta\beta'$ -Dichlorodiethyl Sulphide.** ALBERT ERIC CASHMORE (*T.*, 1923, 123, 1738—1745).

**$\alpha\beta$ -Ethylene Sulphides.** MARCEL DELÉPINE and SIMON ESCHENBRENNER (*Bull. Soc. chim.*, 1923, [iv], 33, 703—711).—

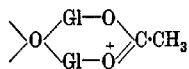
Ethylene sulphide,  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{S}$ , and its homologues behave in a similar

manner to ethylene oxide in many reactions. Nitric acid oxidises ethylene sulphide to sulphoacetic acid,  $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and an acid  $\text{SO}_3\text{H}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and one-third of the sulphur in the original sulphide appears as sulphuric acid in the products of the reaction. Acetic acid condenses with ethylene sulphide to form a white, insoluble powder, which, however, contains only 7.4% of acetic acid as against 50% required for combination in equimolecular proportions. Ammonia and pyridine give products of unknown constitution. Excess of hydrochloric acid yields three products from ethylene sulphide: (a)  $\beta$ -chloroethyl mercaptan,  $\text{HS}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , a colourless, mobile liquid of mercaptan-like odour, b. p.  $43^\circ/13$  mm.,  $60^\circ/25$  mm.,  $d_4^{25}$  1.193,  $n_D^{25}$  1.514; (b) the chlorohydrin,  $\text{HS}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot[\text{CH}_2]_2\text{Cl}$ , a colourless, feebly odorous liquid, b. p.  $120\text{—}127^\circ/20$  mm.; and (c) the compound  $\text{S} < \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} > \text{S}$ , m. p.  $111^\circ$ , subliming at  $127^\circ$ . By the action of iodine, (a) is converted into  $\beta\beta'$ -dichlorodiethyl disulphide, which, in turn, can be oxidised by means of fuming nitric acid to  $\beta$ -chloroethanesulphonic acid. (a) will also condense with acetone in the presence of hydrogen chloride to give the corresponding  $\beta\beta$ -di( $\beta$ -chloroethyl-thiol)-propane,  $\text{CMe}_2(\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$ , an unstable liquid, b. p.  $52\text{—}60^\circ/23$  mm. (decomp.). Oxidation of this compound with cold acid permanganate yields the sulphonol derivative  $\beta\beta$ -di( $\beta$ -chloroethylsulphone)propane,  $\text{CMe}_2(\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$ , as white, nacreous crystals, softening at  $60^\circ$ , m. p.  $68\text{—}69^\circ$ . Aqueous hydrobromic acid combines with ethylene sulphide to give  $\beta$ -bromoethyl mercaptan, an unstable, colourless liquid, denser than water. Similarly, hydrochloric acid combines with butylene sulphide to give chlorobutane-thiol, b. p.  $61^\circ/23$  mm.,  $d$  1.07.

H. H.

**Electrolytic Oxidation of Formic Acid.** ERICH MÜLLER (*Z. Elektrochem.*, 1923, 29, 264—274).—The author has investigated the electrolytic anodic oxidation of formic acid in solutions acidified with sulphuric acid, and the electrolysis of neutral and alkaline solutions of sodium formate, employing a platinum cathode and an anode of platinum, rhodium, palladium, or iridium. Applying a gradually increasing polarising  $E.M.F.$  between the electrodes, it was found that oxidation of formic acid to carbon dioxide and water occurred at a very low value of the anode potential, of the order 0.1 volt, and after attaining a maximum value decreased to a minimum and then increased rapidly when the anode potential attained a value of the order 1 volt. It is concluded that oxidation is effected in two different ways. The first is effected by a small applied  $E.M.F.$  when a catalyst metal is present, and the second, necessitating the use of a large  $E.M.F.$ , is operative when the metal is covered with a layer of oxide. The oxidation of formic acid to carbon dioxide and hydrogen was not definitely established. J. S. G. T.

**The Structure of Basic Glucinum Acetate.** N. V. SIDOWICK (*Nature*, 1923, **111**, 808—809).—A formula is proposed for the compound  $\text{Gl}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ , the crystal structure of which has been described by Bragg (this vol., i, 532). The attachment of



the acetate group to two glucinum atoms, as in the annexed scheme, results in the production of a stable 6-ring, in the formation of which each acetate group loses an electron from its carbonyl oxygen; these six electrons, in addition to two given up by the central oxygen atom, increase the valency electrons of each glucinum atom from two to four. Thus each glucinum atom can form four non-polar links: (1) to the central oxygen atom, and (2), (3), (4) through three acetate groups to each of the other three glucinum atoms, one of these six chelate groups thus corresponding with each edge of the tetrahedron (cf. Tanatar and Kuroski, *A.*, 1907, i, 888; 1908, i, 166, 758).

A. A. E.

**Action of Carbon Disulphide on Mercuric Acetate.** II A. BERNARDI and G. ROSSI (*Gazzetta*, 1923, **53**, i, 225—228).—With reference to Miolati's remarks (*A.*, 1922, i, 982) on the authors' work (*A.*, 1922, i, 421), it is shown that the compound obtained by Palm and studied by Borelli (*A.*, 1909, i, 452) exhibits physical properties differing markedly from those of the authors' compound

T. H. P.

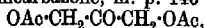
**Lead Tetra-acetate as an Oxidising Agent.** OTTO DIMBORTI and ROBERT SCHWEIZER (*Ber.*, 1923, **56**, [B], 1375—1385).—Lead tetra-acetate is a very efficient agent for the conversion of the hydrogen atom into the hydroxyl group, particularly in the case of substances such as ethyl malonate and ethyl acetoacetate which contain a mobile hydrogen atom. It can also be applied to the homologues of benzene, such as toluene, diphenylmethane etc. In general, its use appears to be most successful when it reacts rapidly with the oxidisable substance. Since the concentration of lead tetra-acetate solutions is readily measured volumetrically, it can be used in the titrimetric comparison of the mobility of hydrogen atoms in organic compounds, and may also find application in measuring the additive capacity, of double linkings.

An improved method for the preparation of lead tetra-acetate is described in detail. Its estimation is effected by dissolving about 0.5 g. of the sample in warm glacial acetic acid which has been distilled over permanganate, adding a solution of sodium acetate (12 g.) and potassium iodide (1 g.), and titrating after five minutes with thiosulphate solution. Boiling glacial acetic acid is not completely stable towards lead tetra-acetate, but sufficiently so to enable it to be used as a solvent.

Lead tetra-acetate reacts with boiling acetic anhydride, giving *acetoxyacetic anhydride*,  $\text{O}(\text{CO}\cdot\text{CH}_2\cdot\text{OAc})_2$ , a colourless liquid, b. p. 178—180°/20 mm., lead diacetate, and small quantities of carbon dioxide and ethane.

Acetone is oxidised by lead tetra-acetate in the presence of

glacial acetic acid in accordance with the relative proportions employed either to *acetylcarbonyl acetate*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OAc}$  (identified as the semicarbazone, m. p.  $146^\circ$ ), or the *diacetate*,



colourless needles, m. p.  $46\text{--}47^\circ$  (*semicarbazone*, needles, m. p.  $93^\circ$ ). Acetophenone is somewhat slowly converted into benzoylcarbonyl acetate.

[With O. SCHAAFF.]—Ethyl malonate is transformed into ethyl acetoxy malonate, the identity of which is established by converting it into tartronic acid.

Ethyl acetoacetate, dissolved in glacial acetic acid or, preferably, in benzene or acetic anhydride, is readily oxidised to ethyl acetoxyacetoacetate, a yellow liquid which becomes colourless when preserved, b. p.  $120\text{--}122^\circ/15$  mm. It is decomposed by boiling dilute sulphuric acid into acetol, acetic acid, alcohol, and carbon dioxide. It yields a *semicarbazone*, m. p.  $124^\circ$ , which is decomposed by boiling water. It is converted by an excess of phenylhydrazine into  $\beta$ -acetophenylhydrazide and 4-hydroxy-1-phenyl-3-methylpyrazol-5-one, colourless leaflets, m. p.  $225^\circ$  (decomp.), the constitution of which is established by its further conversion by phenylhydrazine into benzeneazo-1-phenyl-3-methylpyrazol-5-one. In a similar manner, ethyl benzoylacetate is transformed into ethyl  $\alpha$ -acetoxybenzoylacetate, a pale yellow liquid, b. p.  $140\text{--}143^\circ/1$  mm., which is hydrolysed by dilute sulphuric acid to benzoylcarbinol. With an excess of phenylhydrazine, it yields benzeneazo-1:3-diphenylpyrazol-5-one, small red needles, m. p.  $170\text{--}171^\circ$ .

Benzene is very stable towards lead tetra-acetate. Toluene is much more readily attacked with the formation of benzyl acetate. Diphenylmethane in the presence of glacial acetic acid is converted into benzhydryl acetate, m. p.  $40^\circ$ , whereas triphenylmethane is still more easily transformed into triphenylcarbonyl acetate.

Anethole reacts smoothly and readily with lead tetra-acetate, giving the acetate of the two stereoisomeric  $\alpha$ -p-anisylpropane-2-diols.

H. W.

#### Action of Uranyl Acetate on some Organic Substances.

I. Action of Uranyl Acetate on Malic Acid. FRITZ KOPATSCHEK (*Anal. Asoc. Quim. Argentina*, 1922, 10, 318—334; *ibid.*, 1922, i, 984—985).—Uranyl acetate forms an optically active compound with malic acid analogous to that formed with tartaric acid. No compound is formed with lactic acid, and it is suggested that for the reaction hydroxy-acids with four or more carbon atoms are required. The effect of different substances on the reaction is studied.

G. W. R.

Complex Mixed Bismuthobromoacetates. A. C. VOURNAZOS (*Bull. Soc. chim.*, 1923, [iv], 33, 699—702).—Although the parent acid,  $(\text{BiBr}_2\cdot\text{CH}_3\cdot\text{CO}\cdot\text{O})\text{H}$ , was not isolated, several of its salts are quite stable and are readily prepared by adding a solution of bismuth bromide in anhydrous acetic acid to a solution of the appro-

*dd\**

priate base in the same solvent. It is not considered that the compounds are co-ordination complexes, but rather that the bismuth atom is quinquevalent, thus  $\text{Br}_3\text{Bi}(\text{NH}_4)\text{OAc}$  represents the ammonium salt.

The salts of *ammonium* (hexagonal tablets), *potassium* (hexagonal tablets), *sodium* (isomorphous with the potassium salt), *lithium* (microcrystalline precipitate), *methylamine* (brilliant prisms), *ethylamine* (needles), *aniline* (long, hexagonal tablets), and *o-toluidine* (needles and tetragonal prisms) are described. They all exhibit a yellow colour and are decomposed by cold water with the formation of bismuth oxybromide.

H. H.

**Preparation of  $\beta$ -Chloroethyl Acetate.** CHEMISCHE FABRIK KALK G. M. B. H. and HERMANN OEHME (D.R.-P. 362747; from *Chem. Zentr.*, 1923, ii, 405).—Ethylene and chlorine, together or successively, are passed into acetic acid in the presence of suitable solvents.  $\beta$ -Chloroethyl acetate has b. p.  $145^\circ$  and  $d$  1.178.

G. W. R.

**The Katabolism of Hexoic Acid and its Derivatives.** H. D. DAKIN (*J. Biol. Chem.*, 1923, 56, 43—51).—In order to gain information regarding the first stage in the so-called  $\beta$ -oxidation of fatty acids, hexoic acid and its three possible initial oxidation products,  $\Delta^1$ -hexenoic,  $\beta$ -hydroxyhexoic, and butyrylacetic acids have been perfused through a surviving liver. In each case large amounts of acetoacetic acid, acetone, and  $\beta$ -hydroxybutyric acid were produced. The quantitative differences between the products from the various acids were, however, insufficient to indicate which, if any, of the three partly oxidised acids was preferentially produced from hexoic acid. The results suggest that the  $\alpha\beta$ -unsaturated,  $\beta$ -ketonic, and  $\beta$ -hydroxy-acids are readily interconvertible and are present in equilibrium. Perfusion experiments have also been made with sorbic acid; both acetoacetic and  $\beta$ -hydroxybutyric acids were produced, but in much smaller yield than with the above acids. Evidently sorbic acid is not a normal metabolite of hexoic acid.

E. S.

**Olefine-monocarboxylic Acids.** K. VON AUWERS [with TH. MEISSNER, O. SEYDEL, and H. WISSEBACH] (*Annalen*, 1923, 432, 46—84).—Only a few of the homologues of crotonic acid,  $\text{R}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , are known to exist in stereoisomeric forms, perhaps, amongst other reasons, because, although both forms are produced when the acids are made by the usual methods, the violence of the processes used causes conversion of the less stable into the more stable isomeride. A number of unsaturated acids have therefore been prepared by condensing aldehydes with malonic acid in the presence of pyridine at the ordinary temperature, and the products carefully examined for the presence of isomerides. It is concluded that the elimination of water and carbon dioxide from the hydroxy-dicarboxylic acid which is initially produced leads to the formation of the *trans*-form, but not the *cis*-form, of the  $\alpha\beta$ -unsaturated monocarboxylic acid, together with the  $\beta\gamma$ -un-

saturated acid. The yield of the latter is greater the greater the number of atoms in the carbon chain. It is also produced with particular ease when the  $\gamma$ -carbon atom carries a *gem*-dimethyl group. Incidentally, a number of derivatives of unsaturated monocarboxylic acids are described.

Acetaldehyde and malonic acid, in the presence of pyridine, at 0°, in the absence of sunlight, react within twenty-four hours, giving a small quantity of  $\beta$ -hydroxybutyric acid, together with crotonic acid (60%). The latter gives a *p*-bromophenacyl ester,  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$ , glistening leaflets, m. p. 95–96°. The following data are recorded. Freshly prepared isocrotonic acid had m. p. 14.4–14.6°, b. p. 74.4°/15 mm., or 78.2°/18.5 mm.,  $d_4^{20}$  1.0267,  $d_4^{25}$  1.027,  $n_D^{20}$  1.44223,  $n_{\text{H}_2\text{O}}^{20}$  1.44600,  $n_D^{25}$  1.45510,  $n_{\text{H}_2\text{O}}^{25}$  1.46311,  $n_{\text{H}_2\text{O}}^{30}$  1.4460. Ethyl isocrotonate has b. p. 129–130.5°/742 mm.,  $d_4^{20}$  0.9246,  $d_4^{25}$  0.924,  $n_D^{20}$  1.42256,  $n_{\text{H}_2\text{O}}^{20}$  1.42590,  $n_D^{25}$  1.43285,  $n_{\text{H}_2\text{O}}^{25}$  1.43974 at 19.6°,  $n_{\text{H}_2\text{O}}^{30}$  1.4257. *p*-Bromophenacyl isocrotonate forms glistening, elongated leaflets, m. p. 80.5–81.5°. Ethyl  $\alpha$ -chlorocrotonate (cf. A., 1912, ii, 1015; also Eisenlohr, A., 1912, ii, 2) has b. p. 61°/10 mm.,  $d_4^{15}$  1.1073,  $d_4^{20}$  1.102,  $n_D^{20}$  1.45246,  $n_{\text{H}_2\text{O}}^{20}$  1.45580,  $n_D^{25}$  1.46367,  $n_{\text{H}_2\text{O}}^{25}$  1.47063 at 14.3°,  $n_{\text{H}_2\text{O}}^{30}$  1.4532. Ethyl  $\beta$ -chlorocrotonate (*loc. cit.*) has b. p. 66°/10 mm.,  $d_4^{15}$  1.1018,  $d_4^{20}$  1.101,  $n_D^{20}$  1.45639,  $n_{\text{H}_2\text{O}}^{20}$  1.45985,  $n_D^{25}$  1.46836,  $n_{\text{H}_2\text{O}}^{25}$  1.47583 at 19.2°,  $n_{\text{H}_2\text{O}}^{30}$  1.4595. Ethyl  $\alpha$ -chloroisocrotonate, from the silver salt of the acid and ethyl iodide, has b. p. 58°/12 mm., or 75°/30 mm.,  $d_4^{15}$  1.1021,  $d_4^{20}$  1.100,  $n_D^{20}$  1.45068,  $n_{\text{H}_2\text{O}}^{20}$  1.45391,  $n_D^{25}$  1.46171,  $n_{\text{H}_2\text{O}}^{25}$  1.46868 at 18.0°,  $n_{\text{H}_2\text{O}}^{30}$  1.4530. Ethyl  $\beta$ -chloroisocrotonate (*loc. cit.*) has b. p. 50°/10 mm.,  $d_4^{15}$  1.0920,  $d_4^{20}$  1.086,  $n_D^{20}$  1.45317,  $n_{\text{H}_2\text{O}}^{20}$  1.45679,  $n_D^{25}$  1.46561,  $n_{\text{H}_2\text{O}}^{25}$  1.47345 at 14.4°,  $n_{\text{H}_2\text{O}}^{30}$  1.4543. The reaction between malonic acid and propaldehyde, in the presence of pyridine, at the ordinary temperature, gives a small quantity of  $\beta$ -hydroxyvaleric acid, together with  $\Delta^2$ -pentene- $\alpha$ -carboxylic acid, which has b. p. 71°/2 mm., 96°/10 mm., or 108°/17 mm.; a sample purified by distillation in a high vacuum had m. p. 10°,  $d_4^{17}$  0.9947,  $d_4^{20}$  0.990,  $n_D^{20}$  1.44977,  $n_{\text{H}_2\text{O}}^{20}$  1.45370,  $n_D^{25}$  1.46269,  $n_{\text{H}_2\text{O}}^{25}$  1.47068 at 14.7°,  $n_{\text{H}_2\text{O}}^{30}$  1.4513. Since, when the acid is purified by distillation with the aid of a water-pump, the optical exaltations are somewhat low, it is concluded that the isomeric  $\Delta^2$ -unsaturated acid is present in small amount. The acid chloride of the  $\alpha\beta$ -unsaturated acid has b. p. 37°/11 mm.,  $d_4^{20}$  1.0653,  $d_4^{25}$  1.063,  $n_D^{20}$  1.46225,  $n_{\text{H}_2\text{O}}^{20}$  1.46616,  $n_D^{25}$  1.47597,  $n_{\text{H}_2\text{O}}^{25}$  1.48481 at 18.0°,  $n_{\text{H}_2\text{O}}^{30}$  1.4653. The ethyl ester has b. p. 157.6–158°/745 mm., or 48°/11 mm. (cf. Wohlgemuth, A., 1915, i, 116),  $d_4^{20}$  0.9072,  $d_4^{25}$  0.909,  $n_D^{20}$  1.42737,  $n_{\text{H}_2\text{O}}^{20}$  1.43047,  $n_D^{25}$  1.43788,  $n_{\text{H}_2\text{O}}^{25}$  1.44422 at 21.9°,  $n_{\text{H}_2\text{O}}^{30}$  1.4313. This ester readily absorbs two atoms of bromine in carbon disulphide solution, giving ethyl  $\alpha\beta$ -dibromovalerate, which has b. p. 117–117.5°/14 mm.,  $d_4^{20}$  1.6199,  $d_4^{25}$  1.613,  $n_D^{20}$  1.49527,  $n_{\text{H}_2\text{O}}^{20}$  1.49863,  $n_D^{25}$  1.50656,  $n_{\text{H}_2\text{O}}^{25}$  1.51332 at 15.4°,  $n_{\text{H}_2\text{O}}^{30}$  1.4966.  $\Delta^2$ -Pentene- $\alpha$ -carboxylic acid gives a *p*-bromophenacyl ester, which forms colourless leaflets, m. p. 67–68°, and an amide, glistening leaflets, m. p. 148°. The latter readily absorbs bromine in glacial acetic acid solution, giving  $\alpha\beta$ -dibromovaleramide, hard, white needles, m. p. 168° (decomp.). The unsaturated amide is

converted, by distilling with phosphoric oxide under reduced pressure, into  $\Delta^2$ -pentenenitrile, which has b. p.  $36^\circ/10$  mm. (cf. Henry, A., 1899, i, 567),  $d_4^{15}$  0.8311,  $d_4^{20}$  0.828,  $n_D$  1.43134,  $n_D$  1.43472,  $n_D$  1.44308,  $n_D$  1.44988 at  $15.5^\circ$ ,  $n_D^{20}$  1.4327.  $\alpha\beta$ -Dibromovaleronitrile, prepared in an analogous manner, has b. p.  $110$ – $111^\circ/10$  mm.,  $d_4^{15}$  1.7598,  $d_4^{20}$  1.756,  $n_D$  1.51766,  $n_D$  1.52133,  $n_D$  1.53019,  $n_D$  1.53881 at  $17.6^\circ$ ,  $n_D^{20}$  1.5203.  $\Delta^2$ -Pentene- $\alpha$ -carboxylic acid, prepared from methylparaconic acid, had b. p.  $92.5^\circ/15$  mm.,  $d_4^{15}$  0.9941,  $d_4^{20}$  0.995,  $n_D$  1.43237,  $n_D$  1.43615,  $n_D$  1.44200,  $n_D$  1.44796 at  $21.5^\circ$ ,  $n_D^{20}$  1.4368. Another sample, obtained by the reduction of vinylacrylic acid, had b. p.  $94^\circ/16$  mm.,  $d_4^{15}$  0.9885,  $d_4^{20}$  0.987,  $n_D$  1.43285,  $n_D$  1.43569,  $n_D$  1.44248,  $n_D$  1.44821 at  $18.8^\circ$ ,  $n_D^{20}$  1.4352. The *p*-bromophenacyl ester forms glistening leaflets, m. p.  $87$ – $88^\circ$ . The acid chloride has b. p.  $53$ – $54^\circ/55$  mm.,  $d_4^{15}$  1.0666,  $d_4^{20}$  1.064,  $n_D$  1.44716,  $n_D$  1.44990,  $n_D$  1.45733,  $n_D$  1.46383 at  $16.9^\circ$ ,  $n_D^{20}$  1.4485. The amide, glistening leaflets, m. p.  $69$ – $70^\circ$ , reacts with bromine to give an oily product, and is converted, by means of phosphorus pentoxide, into the nitrile (cf. this vol., i, 661), which has b. p.  $75^\circ/74$  mm.,  $d_4^{15}$  0.8423,  $d_4^{20}$  0.841,  $n_D$  1.42084,  $n_D$  1.42358,  $n_D$  1.42998,  $n_D$  1.43547 at  $18.8^\circ$ ,  $n_D^{20}$  1.4230. Tiglic acid has  $d_4^{15}$  0.9427, and hence  $d_4^{20}$  0.9425,  $n_D$  1.42435,  $n_D$  1.42746,  $n_D$  1.43629,  $n_D$  1.44407 at  $99.7^\circ$ . The ethyl ester of tiglic acid has b. p.  $55.5^\circ/11$  mm.,  $64^\circ/17$  mm., or  $80.5$ – $81.5^\circ/45$  mm.,  $d_4^{15}$  0.9247,  $d_4^{20}$  0.924,  $n_D$  1.43236,  $n_D$  1.43534,  $n_D$  1.44290,  $n_D$  1.44927 at  $19.5^\circ$ ,  $n_D^{20}$  1.4353. Angelic acid has  $d_4^{15}$  0.9298, and hence  $d_4^{20}$  0.9295,  $n_D$  1.41674,  $n_D$  1.41998,  $n_D$  1.42846,  $n_D$  1.43593 at  $100^\circ$ , and its ethyl ester has b. p.  $48.5$ – $49.5^\circ/11$  mm.,  $58$ – $59^\circ/18$  mm., or  $72$ – $73^\circ/39$  mm.,  $d_4^{15}$  0.9178,  $d_4^{20}$  0.917,  $n_D$  1.42781,  $n_D$  1.43102,  $n_D$  1.43802,  $n_D$  1.44435 at  $19.5^\circ$ ,  $n_D^{20}$  1.4308. Ethyl  $\beta\beta$ -dimethylacrylate has  $d_4^{15}$  0.9171,  $d_4^{20}$  0.913,  $n_D$  1.43335,  $n_D$  1.43679,  $n_D$  1.44462,  $n_D$  1.45177 at  $15.0^\circ$ ,  $n_D^{20}$  1.4345.  $\beta\beta$ -Dimethylacrylyl chloride has b. p.  $145$ – $147^\circ$ ,  $d_4^{15}$  1.0632,  $d_4^{20}$  1.058,  $n_D$  1.47479,  $n_D$  1.47980,  $n_D$  1.49137,  $n_D$  1.50231, at  $12.35^\circ$ ,  $n_D^{20}$  1.4763.  $\beta\beta$ -Dimethylacrylamide forms white needles, m. p.  $65$ – $66^\circ$ .  $\Delta^2$ -Hexene- $\alpha$ -carboxylic acid has  $d_4^{15}$  0.9490,  $d_4^{20}$  0.955,  $n_D$  1.44360,  $n_D$  1.44666,  $n_D$  1.45538,  $n_D$  1.46287 at  $40.0^\circ$ ,  $n_D^{20}$  1.4557, and its ethyl ester has b. p.  $80.0$ – $80.2^\circ/14$  mm., or  $93.4$ – $93.8^\circ/31$  mm.,  $d_4^{15}$  0.9005,  $n_D$  1.43165,  $n_D$  1.43474,  $n_D$  1.44200,  $n_D$  1.44849 at  $20.0^\circ$ .  $\Delta^2$ -Hexene- $\alpha$ -carboxyl chloride has b. p.  $41$ – $42^\circ/12$  mm. (cf. Ott and Zimmermann, A., 1922, i, 137),  $d_4^{15}$  1.0142,  $d_4^{20}$  1.014,  $n_D$  1.44405,  $n_D$  1.44730,  $n_D$  1.45455,  $n_D$  1.46038 at  $19.6^\circ$ ,  $n_D^{20}$  1.4471, and the amide, white leaflets, has m. p.  $60^\circ$ . The nitrile is prepared from the latter, and has b. p.  $103$ – $104^\circ/91$  mm.,  $d_4^{15}$  0.8424,  $d_4^{20}$  0.841,  $n_D$  1.43023,  $n_D$  1.43313,  $n_D$  1.43980,  $n_D$  1.44557 at  $18.0^\circ$ ,  $n_D^{20}$  1.4322. The condensation of isobutaldehyde with malonic acid gives  $\beta$ -hydroxy- $\gamma$ -methylbutane- $\alpha$ -carboxylic acid and  $\gamma$ -methyl- $\Delta^2$ -butene- $\alpha$ -carboxylic acid, together with an appreciable quantity of the  $\Delta^2$ -acid. The  $\Delta^2$ -unsaturated acid may be purified by repeated distillation, and has b. p.  $106$ – $108^\circ/12$  mm.,  $d_4^{15}$  0.9589,  $d_4^{20}$  0.955,  $n_D$  1.44706,  $n_D$  1.45060,  $n_D$  1.45931,  $n_D$  1.46689 at  $16.0^\circ$ ,  $n_D^{20}$  1.4488. Its ethyl ester has b. p.

55–56°/9 mm.,  $d_4^{20}$  0.8971,  $d_4^{25}$  0.896,  $n_D$  1.43043,  $n_{He}$  1.43363,  $n_D$  1.44079,  $n_D$  1.44704 at 18.5°,  $n_{He}^{20}$  1.4329. The *p*-bromophenacyl ester forms white leaflets, m. p. 71–72°. The acid chloride has b. p. 53–54°/12 mm.,  $d_4^{15}$  1.0235,  $d_4^{20}$  1.018,  $n_D$  1.45994,  $n_{He}$  1.46396,  $n_D$  1.47348,  $n_D$  1.48185 at 14.2°,  $n_{He}^{20}$  1.4614. The amide forms white leaflets, m. p. 82–86° (indefinite). The nitrile has b. p. 43–44°/11 mm. (cf. Henry, A., 1899, i, 256),  $d_4^{20}$  0.8258,  $d_4^{25}$  0.823,  $n_D$  1.43245,  $n_{He}$  1.43574,  $n_D$  1.44367,  $n_D$  1.45039 at 16.5°,  $n_{He}^{20}$  1.4342.  $\alpha$ -Bromo- $\alpha$ -ethylbutyryl bromide (Rassow and Bauer, A., 1909, i, 758) has b. p. 83°/13 mm. The solid  $\alpha$ -ethylcrotonic acid has  $d_4^{20}$  0.9484,  $n_D$  1.44022,  $n_{He}$  1.44260,  $n_D$  1.45102,  $n_D$  1.45842 at 56.1°, and its ethyl ester has  $d_4^{20}$  0.9106,  $d_4^{25}$  0.908,  $n_D$  1.43407,  $n_{He}$  1.43705,  $n_D$  1.44438,  $n_D$  1.45069 at 17.0°,  $n_{He}^{20}$  1.4357. The amide forms white leaflets, m. p. 114–115° (cf. Mannich and Zernik, A., 1908, i, 399). The liquid  $\alpha$ -ethylcrotonic acid has  $d_4^{20}$  0.9805,  $d_4^{25}$  0.976,  $n_D$  1.45017,  $n_{He}$  1.45337,  $n_D$  1.46170,  $n_D$  1.46881 at 15.0°,  $n_{He}^{20}$  1.4511, and its ethyl ester has b. p. 158–159°,  $d_4^{20}$  0.9042,  $d_4^{25}$  0.899,  $n_D$  1.42779,  $n_{He}$  1.43060,  $n_D$  1.43749,  $n_D$  1.44320 at 13.9°,  $n_{He}^{20}$  1.4279. Ethyl  $\alpha\beta\beta$ -trimethylacrylate has  $d_4^{20}$  0.9244,  $d_4^{25}$  0.921,  $n_D$  1.44259,  $n_{He}$  1.44579,  $n_D$  1.45353,  $n_D$  1.46047 at 16.0°,  $n_{He}^{20}$  1.4440. When the condensation of isovaleraldehyde with malonic acid, in the presence of pyridine, is conducted at the ordinary temperature, the products are  $\beta$ -hydroxyisheptonic acid and  $\delta$ -methyl- $\Delta^4$ -pentene- $\alpha$ -carboxylic acid; if the reaction is carried out at 100°, the  $\Delta^2$ -unsaturated acid is also produced in a comparatively large quantity. Three samples of the  $\Delta^4$ -acid are described. The first had been purified by freezing and had  $d_4^{20}$  0.9458,  $d_4^{25}$  0.942,  $n_D$  1.45118,  $n_{He}$  1.45460,  $n_D$  1.46328,  $n_D$  1.47034 at 15.3°,  $n_{He}^{20}$ . This material, after distillation, had  $d_4^{20}$  0.9444,  $d_4^{25}$  0.941,  $n_D$  1.45087,  $n_{He}$  1.45441,  $n_D$  1.46289,  $n_D$  1.47036 at 16.0°,  $n_{He}^{20}$  1.4526. The third sample had been purified through the calcium salt, with subsequent distillation under reduced pressure, and had b. p. 123–124°/15 mm.,  $d_4^{20}$  0.9464,  $d_4^{25}$  0.942,  $n_D$  1.45146,  $n_{He}$  1.45520,  $n_D$  1.46367,  $n_D$  1.47096 at 14.5°,  $n_{He}^{20}$  1.4527. The ethyl ester has b. p. 190°,  $d_4^{20}$  0.8930,  $d_4^{25}$  0.889,  $n_D$  1.43538,  $n_{He}$  1.43845,  $n_D$  1.44576,  $n_D$  1.45226 at 15.2°,  $n_{He}^{20}$  1.4363. The *p*-bromophenacyl ester forms white leaflets having a silky lustre, and has m. p. 87–88°. The acid chloride has b. p. 64°/12 mm.,  $d_4^{15}$  0.9940,  $d_4^{20}$  0.991,  $n_D$  1.45887,  $n_D$  1.46259,  $n_D$  1.47202,  $n_D$  1.48011 at 17.1°,  $n_{He}^{20}$  1.4613. The amide forms white, lustrous scales, m. p. 127–128°, and reacts with bromine in glacial acetic acid solution in the presence of sunlight, giving  $\alpha\beta$ -dibromoisohexoamide, glistening, white needles, b. p. 169–170°. The  $\Delta^2$ -unsaturated nitrile has b. p. 65°/13 mm.,  $d_4^{20}$  0.8286,  $d_4^{25}$  0.823,  $n_D$  1.44020,  $n_{He}$  1.44346,  $n_D$  1.45132,  $n_D$  1.45807 at 12.0°,  $n_{He}^{20}$  1.4399.  $\Delta^4$ -Nonene- $\alpha$ -carboxylic acid, prepared from heptaldehyde and malonic acid, and purified through the barium salt (Harding and Weizmann, T., 1910, 97, 299) has b. p. 93–94°,  $d_4^{20}$  0.932,  $n_D$  1.45398,  $n_{He}$  1.45730,  $n_D$  1.46473,  $n_D$  1.47124 at 17.1°,  $n_{He}^{20}$  1.4560. A second sample has been prepared by condensing heptaldehyde with ethyl bromoacetate and zinc in

benzene solution, dehydrating the hydroxy-ester by means of sodium hydrogen sulphate, and hydrolysing the unsaturated ester by means of 20% sulphuric acid. For this sample the values quoted are  $d_4^{20}$  0.9334,  $d_4^{25}$  0.930,  $n_D^{20}$  1.45267,  $n_{He}^{20}$  1.45581,  $n_D^{25}$  1.46318,  $n_D^{25}$  1.46956 at 15.6°,  $n_{He}^{25}$  1.4538. The ethyl ester (*loc. cit.*) has b. p. 114—115°/12 mm.,  $d_4^{20}$  0.8901,  $d_4^{25}$  0.889,  $n_D^{20}$  1.43972,  $n_{He}^{20}$  1.44263,  $n_D^{25}$  1.44946,  $n_D^{25}$  1.45544 at 19.0°,  $n_{He}^{25}$  1.4422. The acid chloride (*loc. cit.*) has b. p. 90—91°/12 mm.,  $d_4^{20}$  0.9675,  $d_4^{25}$  0.967,  $n_D^{20}$  1.45738,  $n_{He}^{20}$  1.46075,  $n_D^{25}$  1.46876,  $n_D^{25}$  1.47608 at 19.2°,  $n_{He}^{25}$  1.4604. The amide (*loc. cit.*) has m. p. 118—119°, and is converted in the usual way into the nitrile, which has b. p. 99—100°/10 mm.,  $d_4^{20}$  0.8365,  $d_4^{25}$  0.833,  $n_D^{20}$  1.44454,  $n_{He}^{20}$  1.44758,  $n_D^{25}$  1.45483,  $n_D^{25}$  1.46086 at 15.1°,  $n_{He}^{25}$  1.4454. W. S. N.

### Metallic Hydroxy-acid Complexes. I. Cuprilactates.

IAN WILLIAM WARK (T., 1923, 123, 1815—1826).

### Catalytic Hydrogenation of Castor Oil and its Derivatives.

**Dehydrogenation of the Hydro-oil.** ANDRÉ BROCHET (*Bull. Soc. chim.*, 1923, [iv], 33, 626—632).—Castor oil was readily hydrogenised at 100—120°, employing an active nickel catalyst and hydrogen at 10—12 atm. pressure. The maximum absorption was about 70 c.c. of hydrogen per g. of oil, and the product was a solid fat m. p. 86°, iodine value 2. Methyl ricinoleate prepared by the methanolysis of castor oil, was readily hydrogenised in a similar way at 105—106°, with formation of methyl  $\lambda$ -hydroxystearate, m. p. 55°, and free ricinoleic acid gave a crude hydroxystearic acid, m. p. 75°. The pure  $\lambda$ -hydroxystearic acid was obtained by hydrolysis of the methyl ester. It melted at 81°. When the hydrogenised castor oil was heated with the catalyst at temperatures above 150°, progressively increasing dehydrogenation occurred, reaching a maximum at 270—280°. The product finally obtained did not correspond with the original castor oil, but was a soft semi-solid, m. p. 74°, iodine value 20. G. F. M.

### Decomposition of the Oxalates on Heating in a Vacuum

**I. Lead Oxalate.** JOSEF SVĚDA (*Chem. Listy*, 1923, 17, 47—50, 81—84, 112—114).—Tanatar (A., 1901, ii, 451) and Herschkowitsch (A., 1921, i, 495) stated that the product of the decomposition of lead oxalate on heating at 300° is a suboxide of lead  $Pb_2O$ , whilst Maumené took this product to be a mixture in molecular proportions of lead and litharge. In order to decide this question, lead oxalate is heated at 280—300° in a vacuum obtained by means of a mercury pump, and the evolved gases are collected and analysed. They consist at this temperature of 70% of carbon dioxide and 30% of carbon monoxide, whilst the residue contains 65% of litharge and 35% of lead. The above figures for the gases would correspond with the equation  $2PbC_2O_4 \rightarrow Pb_2O + 3CO + CO_2$ . These relations are, however, altered by conducting the decomposition at 330—370°, and again by heating at 350—400°, owing to reduction of litharge by carbon monoxide. An abnormally high value which was in some cases obtained for the residue

explained by the absorption by the latter of mercury vapour present in the atmosphere. The relative density of the residue is intermediate between those of lead and litharge, and measurements of the heat of solution in acetic acid indicate that the residue consists solely of lead and litharge. The decomposition of lead oxalate hence concluded to consist of the following processes:  $\text{PbC}_2\text{O}_4 \rightarrow \text{PbO} + \text{CO}_2 + \text{CO}$ ,  $\text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2$ , and the formation of  $\text{H}_2\text{O}$  under these conditions is definitely disproved. R. T.

**$\beta$ -Hydroxyglutarodinitrile,  $\beta$ -Bromoglutarodinitrile, and Itaconodinitrile.** R. LESPIEAU (*Bull. Soc. chim.*, 1923, [iv], 3, 725–733).—Partly an account of work already published (this *pl.*, i, 447). *Glutaconodinitrile*,  $\text{CN}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CN}$ , crystallises in prisms, m. p.  $31.5^\circ$ , b. p.  $129\text{--}130^\circ/12\text{ mm.}$ , and is obtained by dehydrating  $\beta$ -hydroxyglutarodinitrile by distillation in a vacuum with phosphoric oxide. A specimen, m. p.  $27^\circ$ , had  $d^{20}_D$  1.0302 and  $n^{20}_D$  1.469 in the superfused state. This nitrile is difficult to hydrolyse to the corresponding acid, but hydrolysis may be effected with aqueous potassium hydroxide on the water-bath. *Ethyl  $\beta$ -hydroxyglutarate* is obtained by hydrolysis of the corresponding nitrile by means of sulphuric acid in the presence of ethyl alcohol. This ester boils at  $150\text{--}153^\circ/16\text{ mm.}$ , and has  $d^{20}_D$  1.10 and  $n^{20}_D$  1.444. *Ethyl  $\gamma$ -cyano- $\beta$ -hydroxybutyrate*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is prepared by hydrolysis and esterification of the corresponding chloronitrile, and then acting on the resulting ester with potassium cyanide. It is a liquid, b. p.  $155\text{--}157^\circ/10\text{ mm.}$ ,  $d^{20}_D$  1.1257,  $n^{20}_D$  1.451. H. H.

**A Much-delayed Correction.** CH. M. VAN DEVENTER (*Chem. Veekblad*, 1923, 20, 331).—In the original papers by J. H. van't Hoff and the author (A., 1886, 968), the discovery of sodium ammonium racemate is incorrectly ascribed to Staedel (A., 1879, 23); it was, in fact, first prepared by Fresenius (*Annalen*, 1842, 1, 9), and the crystal form correctly described by Scacchi (*Rendiconti*, Naples, 1865). S. I. L.

**Polarimetric Observations on Potassium Antimonyl Tartrate, and on Uranyl Tartrate and Malate.** E. DARMOIS (*Compt. rend.*, 1923, 177, 49–51).—It is known that when a solution of potassium antimonyl tartrate is slowly treated with potassium hydroxide, antimony trioxide is precipitated, 96% of the total antimony appearing in this form when a certain amount of alkali has been added. The precipitate redissolves in excess of the reagent, and was formerly supposed to pass into potassium antimonite. A study of the rotatory power, however, indicates that actually it passes into a new laevorotatory substance containing, in addition, potassium and a tartaric acid residue.

Uranyl tartrate, regarded hitherto either as a neutral salt or as a complex acid, is shown, from its behaviour with bases, to be a substance of the latter type. The existence of a disodium salt (unstable in dilute solutions) is deduced from measurements of its rotatory power. Similar results, indicating the existence of a

disodium salt, were obtained with uranyl malate (cf. Itzig, A., 1902, i, 259). E. E. T.

**Metallic Hydroxy-acid Complexes. II. Cuprimalates. Their Formation, Properties, and Composition.** LAN WILLIAM WARK (T., 1923, 123, 1826—1840).

**Constitutional Studies in the Monocarboxylic Acids derived from Sugars. I. Tetramethyl Galactonolactone and the Structure of Galactose.** JOHN PRYDE (T., 1923, 123, 1808—1815).

**The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. III. The Action of Oxygen on Mixtures of Methane and Ethylene and their Oxidation Products.** T. SHERLOCK WHEELER and E. W. BLAIR (J. Soc. Chem. Ind., 1923, 42, 260—266t).—Continuing previous work in which methane and ethylene were studied (A., 1922, i, 1106; 1923, i, 285), the slow oxidation of coal gas has now been investigated, this gas being a natural mixture of methane and ethylene with two of its oxidation products, hydrogen and carbon monoxide. The washed gas was diluted with nitrogen and mixed with a quantity of oxygen insufficient to form an explosive mixture. It was then passed through a tube heated at temperatures between 400° and 720° in different experiments, the time of heating varying between 0.8 and 2.4 secs. The gas was analysed before and after heating. As the temperature rises, first one and then another constituent is oxidised and the rates of reaction rapidly increase until they appear to attain a constant ratio to one another. Hydrogen is first attacked, then methane, and then carbon monoxide; under conditions which cause the decomposition of formaldehyde, water and carbon monoxide are the chief products. The rapid increase in the rate of oxidation of carbon monoxide explains the presence of carbon dioxide in the products at high temperatures. The yield of formaldehyde in these experiments was lower than that obtained from methane only, probably because the ethylene present gives a lower yield. Decomposition of formaldehyde may be induced by the simultaneous oxidation of hydrogen and carbon monoxide. The effect of temperature and other conditions on the yield was similar to that observed in experiments with methane. The effect of surfaces and catalysts was also investigated. Ignited pumice at 510° causes complete oxidation of hydrogen and carbon monoxide, but the hydrocarbons are only slightly attacked; at higher temperatures these are oxidised. Ferric oxide has a similar action, but in addition it causes decomposition of formaldehyde. When the gas is passed over ferric oxide at 400° without addition of oxygen, hydrogen and carbon monoxide are oxidised exclusively, the hydrocarbons not at all. It is suggested that a method of partial combustion for gas analysis might be based on this observation. The catalytic effect of mercury is small. E. H. R.

**Preparation of Formaldehyde.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE, G. M. B. H. (Brit. Pat. 178842).—Formalde-

hyde is produced by passing acetaldehyde vapour mixed with air or oxygen over heated catalysts such as copper, silver, gold, cadmium, lead, bismuth, iron, cobalt, nickel, platinum, or metallic oxides which have several grades of oxidation. Thus when a stream of air containing 1 kg. of acetaldehyde per cu. metre is passed over a coil of copper wire netting at the rate of 500 c.c. per sq. cm. cross section per minute, flameless combustion occurs, and a solution of formaldehyde collects in the receiver amounting in yield to about 50% of the acetaldehyde employed. The process can be carried out in the presence of steam or other indifferent gases or vapours.

G. F. M.

**The Catalytic Synthesis of the Acetals and their Halogenation.** JOSEPH S. REICHERT, JAMES H. BAILEY, and J. A. NIJWLAND (*J. Amer. Chem. Soc.*, 1923, 45, 1552—1557).—Dimethylacetal and diethylacetal are prepared by passing acetylene into the corresponding alcohol in the presence of concentrated sulphuric acid and mercuric sulphate, the yields being 25–30% and 30–35%, respectively. Propyl, isopropyl, butyl, isobutyl, allyl, and amyl alcohols give a very small yield of the corresponding acetals. The rate of absorption of acetylene by the mixture of alcohol, acid, and catalyst decreases with increasing molecular weight of the alcohol. The normal alcohols react more rapidly than the secondary isomerides. The rate of absorption of acetylene is proportional to the amount of catalyst used. The chlorination of dimethylacetal leads primarily to the formation of methyl  $\alpha\beta$ -dichloroethyl ether, with production of methyl alcohol, which is converted into formaldehyde, monochlorodimethyl ether, trioxymethylene, and *s*-dichlorodimethyl ether. The bromination of dimethylacetal leads to the production of formaldehyde, water, hydrobromic acid, methyl alcohol, monobromodimethyl ether, methyl  $\alpha\beta\beta$ -tetrabromoethyl ether, methyl  $\alpha\beta\beta$ -tribromoethyl ether, and *s*-dibromodimethyl ether. Chloral is obtained by the chlorination, preferably at 60–80°, of diethylacetal, or of the partly neutralised liquid from the preparation of diethylacetal by the catalytic process described.

W. S. N.

**Action of Formic Acid on Ethylglycerol [Pentane- $\alpha\beta\gamma$ -triol]. Conversion into  $\beta$ -Ethylacetaldehyde.** RAYMOND DELABY (*Compt. rend.*, 1923, 176, 1898—1901).—If ethylglycerol is boiled with two and a half times its weight of 96–100% formic acid, a mixture (b. p. 150–152°/15 mm.) of the unchanged triol and its formic esters is obtained (on cooling, the *tri-formate* separates in needles, m. p. 60–61°). At 270°, the mixture is converted into ethylvinylcarbinol (b. p. 114–116°),  $\Delta^2$ -penten- $\alpha$ -ol (b. p. 139–140°,  $d_4^{20}$  0.864,  $d_4^{25}$  0.855,  $n_D^{25}$  1.4378), and the formic esters of these alcohols. The new pentenol forms an *allophanate*,  $C_7H_{12}O_3N_2$ , m. p. 157–157.5°, is oxidised by chromic acid mixture to propionic and oxalic acids, whilst cautious oxidation by chromic acid gives the aldehyde,  $CH_3CH:CH\cdot CHO$  (b. p. 126–130°,  $d_4^{20}$  0.867,  $d_4^{25}$  0.854,  $n_D^{25}$  1.4387) which forms a *semicarbazone*, m. p. 177–178°. Silver oxide converts ethylacetaldehyde into ethylacrylic acid. E. E. T.

**The Correlation of Additive Reactions with Tautomeric Change. I. The Aldol Reaction.** EDITH HILDA USHERWOOD (T., 1923, 123, 1717—1726).

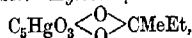
**Influence of Hydrogen Chloride on the Enolising Action of Grignard's Reagent.** VINAYAK KESHAV BHAGWAT (T., 1923, 123, 1803—1807).

**Oximes.** ALICJA DORABIAŃSKI (*Nowy Zjazd Chemików Polskich*, 1923, 25; cf. 1922, A., ii, 548).—Methylglyoxime is shown to exist in two stereoisomeric forms, m. p. 132° and 151°, which may be converted one into the other with great facility. Thermal analysis of methylglyoxime appears to point to the existence of a condition of unstable equilibrium of the oximino-groups, thus militating against the Hantzsch-Werner theory. R. T.

**The Oxidation of Dextrose by Yellow Mercuric Oxide. Preparation of Gluconic Acid.** LÉONCE BERT (*Bull. Soc. chim.*, 1923, [iv], 33, 733—734; cf. this vol., i, 539, and A., 1889, 857).—The formation of mercurous gluconate when dextrose is boiled with mercurous oxide occurs only when the latter is freshly prepared. The results obtained by Blanchetière (this vol., i, 539) are probably due to the fact that he used old preparations of mercuric oxide. [Cf. *J.S.C.I.*, 1923, Aug.] H. H.

**Methyl-ethyl-ketone-xyloses [Xylose sec.-Butylidene Ethers] and Mixed Ketonic Compounds of Xylose.** OLAF SVANBERG and KNUT SJÖBERG (*Ber.*, 1923, 56, [B], 1448—1453).—An extension of previous work (Svanberg and Sjöberg, this vol., i, 540).

Xylose condenses with methyl ethyl ketone in the presence of sulphuric acid with nearly the same readiness as with acetone. The mixture of di- and mono-sec.-butylidene ethers is roughly effected by treatment with light petroleum, in which the former substance is soluble. The final purification is accomplished by distillation in a high vacuum, supplemented in the case of the mono-derivative by solution in water, in which the di-compound is very sparingly soluble. Xylose  $\alpha\beta$ -sec.-butylidene ether,

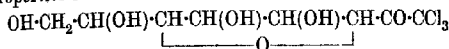


is a liquid, b. p. 127—128°/0—0.5 mm., which occasionally solidifies in the receiver; it has  $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} - 8.0^\circ$  in aqueous solution. Xylose (? $\alpha\beta$ -di-sec.-butylidene ether,  $\text{C}_5\text{H}_9\text{O}(\text{O}_2\text{CMeEt})_2$ , has b. p. 104—106°/0—0.5 mm.,  $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} + 17.4^\circ$  when dissolved in water. It is hydrolysed by dilute hydrochloric acid in much the same manner as xylose diisopropylidene ether. It is readily converted into the mono-derivative by agitation with a quantity of dilute hydrochloric acid which is insufficient for its complete solution. Xylose  $\alpha\beta$ -isopropylidene  $\delta$ (?) -sec.-butylidene ether is a liquid, b. p. 104—105°/high vacuum,  $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} + 16.1^\circ$  ( $\pm 0.5^\circ$ ) in aqueous solution. Xylose  $\delta$ -isopropylidene  $\alpha\beta$ -sec.-butylidene ether is a colourless, viscous liquid, b. p. 102—104°/high vacuum,  $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} + 15.7^\circ$  ( $\pm 0.5^\circ$ ) when dissolved in water.

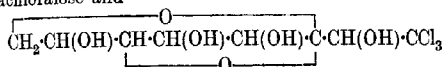
Messenger's method is applicable to the estimation of ketonic groups in *sec.*-butylidene ethers of sugars, a small correction being, however, necessary for the iodine consumed by the carbohydrate.

The observations that the mono*isopropylidene* ethers of xylose are levorotatory, whereas the corresponding di-derivatives are dextrorotatory, appears to invalidate Irvine's application of Hudson's rules (T., 1922, 121, 2146). H. W.

**The Action of Chloral on Glucosans.** AMÉ PICTET and FRANK H. REICHEL (*Helv. Chim. Acta*, 1923, 6, 621—627).—When glucosan is triturated with anhydrous chloral and concentrated sulphuric acid, there are obtained an insoluble substance together with the parachloralose obtained by the action of chloral on dextrose. Levoglucosan, on the other hand, gives the same insoluble substance and chloralose, which is also obtained from chloral and dextrose. It is probable therefore that in the formation of chloralose and parachloralose from dextrose, dehydration of the dextrose first occurs with formation of the two glucosans which react with the chloral before they have time to polymerise. A consideration of their properties leads to the formula



for parachloralose and



for chloralose.

The insoluble substance formed from both glucosan and levoglucosan is a mixture of two substances,  $\text{C}_{10}\text{H}_{10}\text{O}_6\text{Cl}_6$ , called provisionally *isodichloralglucose A* and *B*. They are separated by alcohol, *A* being less soluble. *isoDichloralglucose-A* forms hexagonal lamellae, m. p. 268°; it forms an *acetyl* derivative,  $\text{C}_{12}\text{H}_{12}\text{O}_7\text{Cl}_6$ , m. p. 198°. *isoDichloralglucose-B* is amorphous, m. p. 85°. Neither substance reduces Fehling's solution or potassium permanganate.

E. H. R.

**$\alpha$ -1-Glucosyl-2-glucose.** AMÉ PICTET and JACQUES PICTET (*Helv. Chim. Acta*, 1923, 6, 617—621).—The diglucosan obtained by polymerisation of glucosan (A., 1921, i, 766) should be the anhydride of a disaccharide. By treatment with cold concentrated hydrochloric acid it gave an amorphous, hygroscopic mixture of chlorides which, by treatment with silver carbonate in alcoholic solution, was converted into a mixture of dextrose and a disaccharide. The latter, which is less soluble than dextrose in aqueous alcohol, was separated. It forms an amorphous, hygroscopic powder, containing  $\text{H}_2\text{O}$ , and after dehydrating has m. p. 116—117°. It shows mutarotation,  $[\alpha]_D$  immediately +77.2°; after twenty-four hours +70.2°. It does not give an osazone, and reduces Fehling's solution to the extent of 38.47% as much as dextrose. It is not fermented by emulsin or by brewer's yeast and forms an *octa-acetyl* derivative, apparently cubic crystals, m. p. 85—86°. It gives



**The Nature of "Celloisobiose."** GABRIEL BEERTRAND and (ILL) S. BENOIST (*Compt. rend.*, 1923, 177, 85—87).—The "celloisobiose" of Ost and Prosiegel (A., 1920, i, 423) is shown to be a mixture of cellobiose and procellose (preceding abstract). If the product is extracted systematically with alcohol (70%) for several days, with daily renewal of the solvent, procellose is left, and may be obtained pure by one crystallisation from 85% alcohol.

E. E. T.

**Dextrinozol, the Odorous Constituent of certain Commercial Dextrins, and Ozols in general.** HERMANN KUNZ-RAUSE (*Ber. Deut. pharm. Ges.*, 1923, 33, 149—155).—The characteristic odour of commercial dextrins is conditioned by the presence of a solid, non-volatile constituent, to which the name dextrinozol is given. This appears to be an ester-like compound, either of an unsaturated acid readily convertible into an aliphatic acid with a radicle allied to the terpenes or of an aliphatic or higher dicarboxylic acid with an alcohol radicle of the olefine, acetylene, or terpene series. Treatment of dextrinozol successively with potassium hydroxide solution and hydrochloric acid yields (1) a compound apparently identical with myristic acid, and (2) a compound which is possibly either a phenol analogous to those of the camphor series or a cyclic alcohol.

T. H. P.

**Nature of the Swelling Process. VIII. Reversal of the Swelling of Cellulose Acetate.** E. KNOEVENAGEL (*Koll. Chem. Zeitsch.*, 1923, 18, 39—43; cf. this vol., i, 306).—Cellulose acetate which has been brought into equilibrium in a solvent or mixture of solvents of high swelling power will, when placed in another solvent of lower swelling power, slowly shrink until it comes into equilibrium with the second solvent, that is, until the degree of swelling is that proper for the second solvent. Cellulose acetate which has been swollen to equilibrium with a given solvent when placed in a vacuum over an adsorbent for the swelling liquid gives up the liquid it has adsorbed rapidly at first and then increasingly more slowly. This is shown by the figures 1.0191 g. of cellulose acetate increasing in weight to 1.0656 when swollen with alcohol; after two days in a vacuum the weight fell to 1.0510; seven days, 1.0417; twenty days 1.0386; forty-three days, 1.0361; one hundred and two days, 1.0225. Swelling is a reversible process which comes to an equilibrium value from either side.

J. F. S.

**Soluble Cellulose Esters of the Higher Fatty Acids.** H. AULT and P. EHRMANN (*Compt. rend.*, 1923, 177, 124—127; cf.arrer, Peyer, and Zega, this vol., i, 276).—Hydrocellulose (1 part) readily converted into soluble esters by means of acid chlorides (parts) in presence of an excess of pyridine, using benzene as a solvent and heating at 110—120° for two or three hours. The stearic, dipalmitic, and dilauric esters have been obtained as amorphous substances which are insoluble in water, alcohol, acetone, acetic acid, but soluble in most organic solvents. They do not depress the freezing point of benzene.

E. E. T.

**Lignin and its Relation to Coal.** AMÉ PICTET and MADELEINE GAULIS (*Helv. Chim. Acta*, 1923, 6, 627—640).—Similar reasoning to that which led Fischer and Schrader to put forward the hypothesis that coal is formed from the lignin of wood after the destruction of the cellulose by bacteria (*A.*, 1921, ii, 210) led the authors to study the products of the vacuum distillation of lignin. The lignin (obtained from fir) was distilled at 350—390°/5 to 25 mm. The tar obtained was 15% of the weight of the lignin. From its solution in ether, after extracting with sodium hydroxide solution to remove phenols and acids, a brown oil was obtained amounting to 2% of the weight of the lignin. The oil was separated into saturated and unsaturated hydrocarbons by means of liquid sulphur dioxide and the two fractions were purified by boiling with sodium and fractionally distilled. They consisted entirely of hydroaromatic hydrocarbons. The saturated hydrocarbons gave five fractions having approximately the following compositions: 235—240°,  $C_{13}H_{26}$ ; 260—270°,  $C_{14}H_{26}$ ; 270—280°,  $C_{15}H_{30}$ ; 315—320°,  $C_{24}H_{44}$ ; above 320°,  $C_{30}H_{60}$ . The third fraction appears to be identical with a fraction, 275—285°, from coal tar; the last is identical with melene, a hydrocarbon found in some coal tars and in Galician petroleum. The unsaturated hydrocarbons gave three fractions, 200—210°,  $C_{11}H_{16}$ ; 230—240°,  $C_{12}H_{16}$ ; 250—260°,  $C_{13}H_{16}$ . Of these, the first appears to be identical with a coal tar fraction. The last fraction gives a tetrabromo-derivative,  $C_{13}H_{12}Br_4$ , m. p. 193°; it appears to be related to the hexahydrofluorene of coal tar. These results appear to establish a relationship between lignin tar and coal tar, and to some extent support the hypothesis of Fischer and Schrader. From the phenolic substances of the lignin tar, eugenol was isolated; this observation supports the view that lignin contains the grouping of coniferyl alcohol. The existence of a hydroaromatic ring also follows from the above observations. Lignin contains a high methoxy-group content, 14.19%, and it is now found that lignite contains 3.30% and coal from the Saar 0.79% and from St. Etienne 0.24%, whilst anthracite contains none. The objection to Fischer and Schrader's hypothesis that coal contains no methoxy-group therefore falls to the ground. E. H. R.

**Two "Internal Salts" [Betaine and Taurine].** A. REICHLER (*Bull. Soc. chim. Belg.*, 1923, 32, 247—250).—An examination of some properties of betaine and taurine. (1) Betaine was prepared by heating alcoholic solutions of ethyl chloroacetate and trimethylamine, hydrolysing the product with hydrochloric acid, and treating the betaine hydrochloride obtained (82% yield) with moist silver oxide; the free betaine forms brilliant, deliquescent crystals,  $C_4H_{11}O_2N \cdot H_2O$  (80% yield). (2) Bromoethylphthalimide was heated with concentrated hydrochloric acid for two hours in a sealed tube at 180° and the resultant bromoethylamine hydrochloride solution heated with ammonium sulphite solution; taurine crystallised out partly on cooling, yield about 70%. The molecular weights of betaine hydrochloride determined by cryoscopic

measurements in water lay between one-third and one-half of the theoretical value. The specific electric conductivities in aqueous solution were found to be as follows (the figures in brackets indicate the dilutions in litres): *Betaine*, (2 l.)=0.000013; (4 l.)=0.000011; (8 l.)=0.000009; (16 l.)=0.000009. *Taurine*, (2 l.)=0.000012; (4 l.)=0.000008; (8 l.)=0.000008; (16 l.)=0.000010. *Betaine and taurine in equimolecular amounts*, (2 l.)=0.000019; (4 l.)=0.000012; (8 l.)=0.000011; (16 l.)=0.000011. F. A. M.

**The Bismuthamines, a New Class of Compounds.** A. CH. JOURNAZOS (*Compt. rend.*, 1923, **176**, 1555—1558).—These compounds may be prepared by direct combination of a trivalent bismuth salt with an inorganic or organic ammonium salt, with salts of primary or secondary amines, either aromatic or aliphatic, and with salts of primary hydrazines. Halides of bismuth yield the most characteristic compounds, but they are also given by the trioxide, nitrate, and phosphate. The bismuthamines are of two kinds, simple, in which the bismuth salt and the amine salt are derived from the same acid and mixed, in which derivatives of different acids unite. As most bismuth salts are easily hydrolysed, bismuthamines can only be prepared in organic solvents, and from these they separate in crystalline form. The following are described: *Ammonium bismuthochloriodide*,  $[\text{BiCl}_2\text{I}]\text{NH}_4$ , transparent needles; *ammonium bismuthobromoacetate*,  $[\text{BiBr}_2\text{OAc}]\text{NH}_4$ , yellow, hexagonal tablets; *methylamine bismuthobromoformate*,  $\text{BiBr}_2\cdot\text{NH}_2\text{Me}\cdot\text{HCO}_2\text{H}$ , yellow, prismatic crystals; *ethylamine bismuthiodoacetate*,  $\text{BiI}_2\cdot\text{NH}_2\text{Et}\cdot\text{CH}_3\text{CO}_2\text{H}$ , crimson-scarlet crystals; *methylamine bismuthonitrate*,  $\text{Bi}(\text{NO}_3)_3\cdot\text{NH}_2\text{Me}\cdot\text{NO}_3$ , masses of white crystals; *hydrazine bismuthochloroacetate*,  $\text{BiI}_3\cdot\text{N}_2\text{H}_4\cdot\text{AcOH}$ , colourless prisms; *aniline bismuthofluoroacetate*,  $\text{BiF}_3\cdot\text{NH}_2\text{Ph}\cdot\text{OAc}$ , colourless, prismatic crystals; *aniline bismuthobromoacetate*, pale yellow, hexagonal tablets; *o-toluidine bismuthochloropropionate*,  $\text{BiCl}_3\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{EtCO}_2\text{H}$ , colourless, tetragonal prisms; *n-propylamine bismuthobromobenzoate*,  $\text{BiBr}_3\cdot\text{NH}_2\text{Pr}\cdot\text{PhCO}_2\text{H}$ , tangled, yellow needles. Details of a general method of preparation are given.

H. J. E.

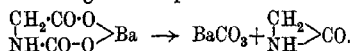
**Hexamethylenetetramine.** RUDOLF PUMMERER and JOSEF HOFMANN (*Ber.*, 1923, **56**, [B], 1255—1259).—Hexamethylenetetramine does not appear to contain a double bond in its molecule, since in aqueous solution it does not unite with hydrogen in the presence of spongy platinum. The observed values for the molecular weight of hexamethylenetetramine are usually somewhat lower than those calculated; in aqueous solution, they are independent of variations in concentration between 1 and 15%. The compound has usually been regarded as a strong base, probably on account of its ability to form well-defined mono-acid salts. It does not, however, redden phenolphthalein; in aqueous solution, it has  $K=2\times 10^{-8}$ .

Hexamethylenetetramine forms additive compounds with three molecular proportions of phenol or of the cresols (the latter compounds are prepared readily by grinding the components together

at the atmospheric temperature in the presence of a few drops of alcohol). Determinations of molecular weight show these compounds to be almost completely resolved into their components when dissolved in water or benzene. On the other hand, measurements of electrolytic conductivity indicate distinctly the formation of salts.

H. W.

**The Action of Dry Heat on the Alkaline-earth Salts of Carbamic Acids.** A. BLANCHETIÈRE (*Compt. rend.*, 1923, 176, 1629—1631).—Specimens of the dry barium salt of carboxylaminoacetic acid were heated at 130°, 150°, and 170°, respectively, and the resulting products examined mainly with a view to determine their respective nitrogen contents. In each case a substance was obtained which is richer in nitrogen than the original amino-acid, and these substances showed extreme readiness to revert in presence of water to the amino-acid from which they were derived. The hypothesis put forward to account for the change is that formation of glycine mixed with its internal anhydride occurs, the latter substance being formed according to the equation



In the case of barium aminopropionate, the results obtained were indefinite.

H. J. E.

**Preparation of  $\alpha$ -Dialkylaminoethyl- $\beta$ -aracylhydroxybutyric Esters.** FARBERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 364038; Swiss Pat. 94324; from *Chem. Zentr.*, 1923, ii, 189—190; cf. A., 1922, i, 639).—Ethyl  $\alpha$ -diethylaminoethylacetate (A., 1922, i, 639) is reduced either with sodium amalgam in weak mineral acid solution or electrolytically, using lead electrodes. Ethyl  $\beta$ -hydroxy- $\alpha$ -diethylaminoethylbutyrate thereby obtained is a colourless liquid, b. p. 135—136°/10 mm. The benzoyl derivative is a colourless oil which gives a hydrochloride, forming colourless needles, m. p. 130—131°. Ethyl  $\beta$ -p-nitrobenzoyl- $\alpha$ -diethylaminoethylbutyrate is an oil which does not solidify. The hydrochloride has m. p. 143°. By reduction it gives the corresponding amino-ester, an oil, which forms a crystalline hydrochloride, m. p. 160°. Phenylcarbimide gives with ethyl  $\beta$ -hydroxy- $\alpha$ -diethylaminoethylbutyrate an oily phenylurethane, the hydrochloride of which has m. p. 136°.

G. W. R.

**Graphical Determination of the Structure of Carbamide and Tin Tetraiodide from Röntgen Ray Analysis.** H. MAX and K. WEISSENBERG (*Z. Physik*, 1923, 16, 1—21).—Independently of chemical and crystallographic characteristics, it is shown that one, and only one, form of crystal lattice in which the atoms can be arranged in one way only, affords a crystal structure in the case of carbamide which is compatible with the Röntgen ray diagram afforded by a crystal of the substance. Urea crystallises in the tetragonal scalenohedral ( $V_8^8$ ) system, with  $a=5.63$  and  $c=4.70$  Å.U. The elementary cell is a simple-primitive structure and

contains two molecules of carbamide. The distance between two nitrogen atoms in the molecule is approximately 2 Å.U.; the distances between the centres of two adjacent molecules is greater than 3.98 Å.U. and less than 4.62 Å.U. In a similar manner, it is shown that tin tetraiodide forms cubical crystals having  $a = 6.04$  Å.U., and that the four iodine atoms in the molecule are arranged tetrahedrally around the tin atom. J. S. G. T.

#### Methylene Derivatives of Succinimide and Phthalimide.

LARIO PASSERINI (*Gazzetta*, 1923, 53, i, 333—338).—The author confirms Bechert's conclusion that the compound, m. p. 290—295°, obtained by the action of trioxymethylene on ethylene cyanide in acetic acid solution containing a little sulphuric acid is methylenesuccinimide (A., 1894, i, 488), and shows that, when hydrolysed gradually, this compound yields first methylenedisuccinamic acid and afterwards ammonia, formaldehyde, and succinic acid; the same compound may be obtained by the action of succinic acid on hexamethylenetetramine. The compound, m. p. 208—209°, obtained by the action of formaldehyde on succinimide in a sealed tube at 150—160°, is not, as Breslau and Pictet state (A., 1907, 915), identical with Bechert's compound, but has the composition  $C_{12}H_{18}O_6N_4$  and the normal molecular weight in freezing naphthalene; it decomposes, yielding succinic acid, formaldehyde (mols.), and ammonia when treated with dilute sulphuric acid, and hence, trisuccinimidotrimethylenamine,  $N(CH_2N \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix})_3$ .

Treatment of hexamethylenetetramine with phthalic acid yields mainly methylenediphtalimide, whilst hexamethylenetetramine and phthalimide give methylphthalimide as principal product.

T. H. P.

#### Peralkylated Guanidine. HANS LECHER and FRITZ GRAF

(*Ber.*, 1923, 56, [B], 1326—1330).—*Pentamethylguanidine*,  $Me_5C(NMe_2)_2$ , is obtained in 35% yield by heating a mixture of methylamine and tetramethyl- $\psi$ -thiocarbamide in the presence of mercuric chloride at 100°. It is a colourless, hygroscopic liquid, b. p. 155—160°, which readily absorbs atmospheric carbon dioxide. It is a strong mono-acid base. The picrate crystallises in yellow needles, m. p. 165—166° (corr. decomp.). It unites readily with ethyl iodide, giving *hexamethylguanidinium iodide*, colourless, crystalline leaflets which remain unchanged below 300°.

Peralkylated guanidines could not be obtained by the action of magnesium ethyl bromide and diethylamine on tetramethylthiocarbamide in the presence of ether or toluene or by the action of dry carbon dioxide or carbon tetrachloride on magnesium ethyl bromide and diethylamine. H. W.

#### Magnetic Properties of Cyanic and Cyanuric Compounds.

PAUL PASCAL (*Compt. rend.*, 1923, 176, 1887—1889).—From a study of the magnetic susceptibilities of compounds of the above types, conclusions are drawn as to the constitution of the compounds. Metallic cyanates appear to possess the isocyanate

structure, whilst cyanuric acid and its salts and ethers are substituted triazines [the acid being written as a centric 6-membered ring composed of three  $\cdot\text{N}\cdot\text{C}(\text{OH})\cdot$  groups in sequence]. Cyanamide, from its (magnetic) resemblance to isocyanurates, is regarded as possessing three  $\cdot\text{O}\cdot\text{C}(\text{NH})\cdot$  groups in sequence in a 6-membered ring; it is therefore the imide corresponding with trioxymethylene.

E. E. T.

**Oxidation of Alkali Cyanides in Aqueous Solution.** LUDWIG HESS (*Ber. Deut. pharm. Ges.*, 1923, 33, 178—181).—The cyanate prepared by oxidising alkali cyanide in aqueous solution by means of sodium hypochlorite (cf. Riedel, A., 1920, i, 156) may be separated in solid form from the solution under suitable conditions. The preparation of the hypochlorite and the oxidation of the cyanide may be effected simultaneously by passing chlorine into a solution of alkali hydroxide and cyanide. Potassium ferri cyanide also serves as a suitable agent to bring about this oxidation.

T. H. P.

**A New Method for the Formation of Cyanates.** W. MARCKWALD and M. WILLE (*Ber.*, 1923, 56, [B], 1325).—According to Raschig (A., 1909, ii, 232), the action of potassium cyanide on chloroamine leads to the production of cyanogen chloride,  $\text{NH}_2\text{Cl} + \text{KCN} + \text{H}_2\text{O} = \text{NH}_3 + \text{CNCl} + \text{KOH}$ . The authors have been unable to confirm this observation; they find that considerable quantities of cyanate are produced.

Potassium cyanate is rapidly produced when equivalent quantities of potassium hypochlorite and potassium cyanide are mixed in aqueous solution.

H. W.

**Butenonitriles. III.** P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1923, 32, 256—269; cf. A., 1922, i, 817, 924).—The action of ammonia or of simple aliphatic amines on vinylacetonitrile leads to the formation of  $\beta$ -amino- or  $\beta$ -alkylamino-butyronitriles, which can be reduced to the corresponding diamines by sodium and alcohol. Fatty amines containing more than three carbon atoms do not form stable additive products, but merely cause isomerisation of the vinylacetonitrile to the crotononitriles.

When vinylacetonitrile is left in contact with an aqueous solution of ammonia for some time at a moderate temperature, the product saturated with potassium carbonate, dried, and distilled under reduced pressure,  $\beta$ -aminobutyronitrile,  $\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CN}$ , is obtained as a mobile liquid with a faintly basic odour, b. p.  $156^\circ/700$  mm. (slight decomp.),  $76\text{--}77^\circ/18$  mm.,  $d_4^{20}$  0.91565,  $n_D^{20}$  1.43283,  $n_D^{20}$  1.43533,  $n_D^{20}$  1.45213. The hydrochloride has m. p.  $157^\circ$ , the chloroplatinate forms golden spangles, m. p.  $236^\circ$  (decomp.), and the benzoyl derivative has m. p.  $118\text{--}119^\circ$ . Reduction of  $\beta$ -aminobutyronitrile with sodium and alcohol yields  $\alpha$ -diaminobutane, b. p.  $139\text{--}141^\circ$ , previously obtained by Tafel (A., 1901, i, 72), the dihydrochloride has m. p.  $169^\circ$ , the dibenzoyl derivative, m. p.  $165\text{--}166^\circ$ .

Hydrolysis of the nitrile with concentrated hydrochloric acid

yields  $\beta$ -aminobutyric acid hydrochloride (*ethyl ester*, b. p. 64—65°/15 mm.), thus proving that the ammonia joins on to the  $\beta$ - and not the  $\gamma$ -carbon atom of the nitrile. A by-product formed in the preparation of the aminonitrile is a colourless basic liquid having the character of a secondary base, b. p. 177°/18 mm., which forms an unstable yellow *nitroso*-derivative. It appears to be *iminodi- $\beta$ -butyronitrile*,  $\text{NH}(\text{CHMe}\cdot\text{CH}_2\cdot\text{CN})_2$ ,  $d_4^{20}$  0.9766,  $n_D^{20}$  1.45654,  $n_D^{20}$  1.45907,  $n_{\text{H}\beta}^{20}$  1.46524. *Chloroplatinate*, deep brown octahedra. The two crotononitriles are also formed as by-products.

With ethylamine, vinylacetonitrile yields  $\beta$ -ethylaminobutyronitrile,  $\text{CH}_3\text{CH}(\text{NEt})\cdot\text{CH}_2\cdot\text{CN}$ , in 80% yield as a colourless liquid with a faint odour, b. p. 192—193°/760 mm. (decomp.), 77—8°/14 mm.,  $d_4^{20}$  0.8763,  $n_{\text{H}\alpha}^{20}$  1.43142,  $n_D^{20}$  1.43372,  $n_{\text{H}\beta}^{20}$  1.43953. The crotononitriles are formed as by-products. The *nitroso*-derivative forms a yellow liquid,  $d_4^{20}$  1.2647. Reduction of  $\beta$ -ethylaminobutyronitrile with sodium and alcohol gives a good yield of  $\alpha$ -amino- $\gamma$ -ethylaminobutane ( $\gamma$ -ethylamino-*n*- $\alpha$ -butylamine),  $[\text{HEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2]$ , as a colourless basic liquid fuming in the air, b. p. 163—164°/753 mm.; the *chloroplatinate* forms fine yellow needles, m. p. 242° (decomp.).

Monomethylamine and vinylacetonitrile yield  $\beta$ -methylaminobutyronitrile,  $\text{NHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 82—83°/16 mm., 183—84°/765 mm. (decomp.); reduced by sodium and alcohol to  $\alpha$ -amino- $\beta$ -methylaminobutane ( $\gamma$ -methylamino-*n*- $\alpha$ -butylamine),  $[\text{HMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2]$ , a colourless, fuming liquid, b. p. 52—53°; the *chloroplatinate* forms clear yellow needles.

Dimethylamine yields with vinylacetonitrile  $\beta$ -dimethylaminobutyronitrile,  $\text{NMe}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CN}$ , in 95% yield, as a colourless, fuming liquid, b. p. 79—80°/13 mm., 186—188°/760 mm., with light decomp.,  $d_4^{20}$  0.88180,  $n_{\text{H}\alpha}^{20}$  1.43338,  $n_D^{20}$  1.4363,  $n_{\text{H}\beta}^{20}$  1.4422. The same product was also obtained by the action of dimethylamine on crotononitrile, thus confirming the position of the amino-group. It was also formed by treating vinylacetonitrile with triethylamine and distilling the product. It unites with ethyl iodide to form the ethiodide, m. p. about 164°, after drying in a vacuum; is unstable and partly liquefies on keeping. On dry distillation, yields the mixed crotononitriles.

Reduction of  $\beta$ -dimethylaminobutyronitrile with sodium and alcohol yields  $\alpha$ -amino- $\gamma$ -dimethylaminobutane ( $\gamma$ -dimethylamino-*n*- $\alpha$ -butylamine),  $\text{NMe}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , which forms a strongly fuming liquid, b. p. 154—156°/753 mm.; it appears to form a hydrate boiling indefinitely between 145° and 155°; the *chloroplatinate*,  $\text{C}_8\text{H}_{16}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$ , forms fine, yellow needles, m. p. 33° (decomp.). A second *chloroplatinate*,  $(\text{C}_8\text{H}_{16}\text{N}_2)_2\cdot 2\text{HCl}\cdot\text{H}_2\text{PtCl}_6$ , as also obtained as pearly yellow spangles, m. p. 245°.

On treatment with magnesium methyl bromide,  $\beta$ -dimethylaminobutyronitrile reacts vigorously with evolution of dimethylamine and formation of a triple polymeride of crotononitrile. On reacting vinylacetonitrile with diethylamine and distilling the product, only a mixture of the crotononitriles was obtained, b. p.

112—115°, and a similar result was observed when using isobutylamine or ethylenediamine. With piperidine, however, a fairly vigorous reaction occurs, and after distilling in a vacuum,  $\beta$ -piperidylbutyronitrile,  $C_5NH_{10}\cdot CHMe\cdot CH_2\cdot CN$ , is obtained as a colourless, odourless liquid, b. p. 126—127°/12 mm.,  $d_4^{20}$  0.9444,  $n_D^{20}$  1.4703,  $n_D^{25}$  1.4727,  $n_D^{30}$  1.4789. On heating at 160°, it dissociates completely into the crotononitriles.

Aromatic amines were found to be without action on vinyl acetone, which could be recovered practically unchanged even, for instance, after heating under reflux with aniline for five hours.

F. A. M.

**iso-Nitriles [Carbylamines]. V. Reaction with Lævulinic Acid.** MARIO PASSERINI (*Gazzetta*, 1923, 53, i, 331—333; cf. this vol., i, 63).—The interaction of lævulinic acid with phenylcarbylamine in ethereal solution results in the formation of the lactone of  $\beta$ -anilino- $\beta$ -hydroxybutane- $\beta\delta$ -dicarboxylic acid, so that in this reaction lævulinic acid behaves as though its structure were  $CH_2\begin{smallmatrix} CH_2\cdot CMe\cdot OH \\ CO-O \end{smallmatrix}$ . This lactone,  $NHPh\cdot CO\cdot CMe\begin{smallmatrix} O-CO \\ CH_2\cdot CH_2 \end{smallmatrix}$ , is a pale yellow, amorphous substance, m. p. 44—46°, and yields aniline and  $\beta$ -hydroxybutane- $\beta\delta$ -dicarboxylic acid on hydrolysis.

T. H. P.

**New Syntheses of Hydrocyanic Acid by means of the Silent Electric Discharge.** L. FRANCESCONI and ADOLFO CIURLO (*Gazzetta*, 1923, 53, i, 327—330).—Under the influence of the silent discharge, a mixture of ethylene and nitrogen undergoes change in accordance with the equations,  $C_2H_4 + N_2 = 2HCN + H_2$  and  $C_2H_4 + HCN = Et\cdot N\dot{C}$ . If a mixture of ethylene and hydrogen cyanide is used, both nitrile and isonitrile are formed:  $C_2H_4 + C\dot{N}\cdot H = Et\cdot N\dot{C}$  and  $C_2H_4 + H\cdot C\dot{N} = Et\cdot C\dot{N}$ . Preliminary experiments with a mixture of acetylene and hydrogen cyanide indicate the formation, in this case also, of both nitrile and isonitrile.

T. H. P.

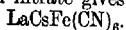
**A New Phototropic Compound of Mercury.** Y. VENKATARAMAIAH and BH. S. V. RAGHAVA RAO (*Nature*, 1923, 111, 775).—Interaction of a mercuric salt with ammonium thiocyanate and thiocarbamide in acetic acid solution in the presence of an oxidising agent, or the action of hydrogen sulphide on mercuric thiocyanate, yields the phototropic compound  $HS\cdot Hg\cdot CNS$ .

A. A. E.

**The Influence of Alkali on the Titration of some Metals with Ferrocyanide.** II. W. D. TREADWELL and D. CHERVET. With a Note by W. D. TREADWELL (*Helv. Chim. Acta*, 1923, 6, 550—559, 559—561).—Using the electrometric method of titration, it has been shown that in ferrocyanides of cadmium, zinc, and lead the heavy metal can be partly displaced by an alkali metal (A., 1922, ii, 786). Continuing this work, it is found that when zinc sulphate is titrated in neutral solution with sodium ferrocyanide, the titration figure corresponds with the ratio  $Zn : Fe(CN)_4 = 2 : 1$ , but in presence of potassium chloride and hydrochloric

acid the ratio is only 1.5 : 1, on account of the formation of a double salt. Similarly, a double salt is formed when a zinc salt is titrated with potassium ferrocyanide in presence of a rubidium salt. Nickel salts behave similarly to those of zinc; with lithium ferrocyanide,  $\text{Ni}_2\text{Fe}(\text{CN})_6$  is formed, with sodium ferrocyanide,  $\text{Ni}_2\text{Na}_2[\text{Fe}(\text{CN})_6]_2$ , and with potassium ferrocyanide, especially in presence of a caesium salt, the precipitate approximates to  $\text{NiK}_2\text{Fe}(\text{CN})_6$ . In the case of cobalt salts, the displacement of the heavy metal by alkali can be followed visually by the change in colour of the precipitate from green to yellow; in composition, the precipitates correspond with those obtained with nickel salts. Owing to the comparatively high solubility of manganese ferrocyanide, manganese salts can only be titrated electrometrically in neutral or weak acetic acid solution. Lithium and sodium ferrocyanides both precipitate  $\text{Mn}_2\text{Fe}(\text{CN})_6$ , whilst potassium ferrocyanide gives  $\text{MnK}_2\text{Fe}(\text{CN})_6$ ; the stage  $\text{Mn}_2\text{K}_2[\text{Fe}(\text{CN})_6]_2$  is not formed. In the case of silver, which forms a ferrocyanide of extremely low solubility, titration with lithium, sodium, or potassium ferrocyanide in the cold gives  $\text{Ag}_4\text{Fe}(\text{CN})_6$ , even in presence of a caesium salt. Addition of excess of ferrocyanide, however, in presence of a caesium salt results in the formation of  $\text{Ag}_2\text{CsFe}(\text{CN})_6$ . The same compound is formed by running the silver solution into potassium ferrocyanide in presence of caesium chloride, but on further addition of silver salt it is wholly converted into  $\text{Ag}_4\text{Fe}(\text{CN})_6$ . The end-point of a titration of sodium ferrocyanide with a silver salt is very clearly marked by the sudden clearing of the cloudy solution caused by the flocculation of the precipitate.

Cerium chloride can be titrated electrometrically with potassium ferrocyanide in presence of caesium chloride, the precipitate being  $\text{Ce}_3[\text{Fe}(\text{CN})_6]_3$ ; lanthanum nitrate gives a precipitate of



NOTE.—The facility with which the alkali metals replace the heavy metals in the ferrocyanides increases from lithium to caesium, that is, with the atomic volume. A similar order is found in the facility of basic exchange of silver by alkali metals in the permittes. This effect is probably due to the decreasing degree of hydration and energy of hydration of the ion of the alkali metal with increasing atomic volume. When the energy necessary for the basic exchange is exceeded by the difference between the energies of hydration of the heavy metal and of the alkali metal, the latter being the smaller, basic exchange will occur. The tendency to exchange must be smaller when, as in the case of silver and lead ferrocyanides, the energy of hydration of the heavy metal approximates to that of the alkali metal.

E. H. R.

**Additive Reactions of Thiocyanogen.** H. P. KAUFMANN and J. LIEPE (*Ber. Deut. pharm. Ges.*, 1923, **33**, 139—148).—The addition of free, especially nascent, thiocyanogen to unsaturated compounds which takes place somewhat less energetically than that of bromine serves as a suitable means of preparing new derivatives of thiocyanogen. Thus 1:2-dithiocyanoethane

(ethylene dithiocyanate) may be prepared by gradual addition of an ethereal solution of iodine to an ethereal suspension of mercuric thiocyanate through which a rapid stream of ethylene is passing, and 1-phenyl-1:2-dithiocyanoethane (styrene dithiocyanate) by adding a solution of lead thiocyanate and bromine in carbon tetrachloride to a solution in the latter of styrene, leaving for six weeks, filtering, and extracting the filtrate with boiling water. Allyl alcohol dithiocyanate (glycerol dithiocyanohydrin) may be obtained by the interaction of allyl alcohol and thiocyanogen in carbon disulphide solution (cf. Engle, A., 1899, i, 39).  $\alpha$ -p-Methoxyphenyl- $\alpha$ - $\beta$ -dithiocyanopropane (anethole dithiocyanate),  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{SCN})\cdot\text{CHMe}(\text{SCN})$ , crystallises in needles, m. p. 87°. isoSafole dithiocyanate,  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2$ , forms crystals, m. p. 109°.

Treatment of ethyl acetoacetate in carbon disulphide solution containing a little alkali with thiocyanogen yields a compound, which is probably the dithiocyano-derivative of the ester but is readily decomposed by moisture, giving ethyl-2-oxo-4-methylthiazole-

5-carboxylate,  $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{CMc}\cdot\text{N} \\ \parallel \\ \text{S}-\text{CO} \end{smallmatrix}$ , crystallising in white needles, m. p. 128°.

1-Thiocyano- $\beta$ -naphthol,  $\text{C}_{11}\text{H}_8\text{ONS}$ , forms crystals, m. p. 68–70°, and slowly decomposes.

1-Thiol- $\beta$ -naphthol,  $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{SH}$ , obtained when the preceding compound is heated with zinc and alcoholic hydrochloric acid, crystallises in long, white needles, m. p. 106°, and, when oxidised by means of hydrogen peroxide, yields dihydroxydi- $\beta$ -naphthyl  $\alpha$ : $\alpha'$ -disulphide (cf. Henriques, A., 1895, i, 104).

1-Thiocyano- $\beta$ -naphthyl methyl ether,  $\text{C}_{12}\text{H}_9\text{ONS}$ , forms white crystals, m. p. 134°, and, when heated with zinc and alcoholic hydrochloric acid, yields

1-Thiol- $\beta$ -naphthyl methyl ether,  $\text{C}_{11}\text{H}_{10}\text{OS}$ , which crystallises in long, white needles, m. p. 98°.

4-Thiocyano- $\alpha$ -naphthol,  $\text{C}_{11}\text{H}_8\text{ONS}$ , is stable in the air, forms crystals, m. p. 85–87°, and, when boiled with zinc and alcoholic hydrochloric acid, yields 4-thiol- $\alpha$ -naphthol (cf. Zincke and Ruppertsberg, A., 1915, i, 135), which yields the corresponding disulphide, m. p. 152°, when oxidised by means of hydrogen peroxide (cf. Zincke and Ruppertsberg, *loc. cit.*). T. H. P.

#### Some Derivatives of Butylarsine: Butylarsinic Acid.

JULES TIFFENEAU (*Bull. Sci. Pharmacol.*, 1922, 29, 440–442; from *Chem. Zentr.*, 1923, i, 508).—*n*-Butylarsine dichloride, prepared from arsenious chloride and mercury *n*-dibutyl (A., 1921, i, 655), is a colourless liquid; it has b. p. 175–180°/760 mm.;  $d_{15}^{15}$  1.54. It is decomposed by alkali hydroxides with formation of *n*-butylarsine oxide,  $\text{C}_4\text{H}_9\text{AsO}$ , a wax-like mass which cannot be distilled without decomposition. Oxidation of *n*-butylarsine chloride gives *n*-butylarsinic acid,  $\text{C}_4\text{H}_9\cdot\text{AsO}(\text{OH})_2$ ; it forms needles, m. p. 158°. Phenyl-*n*-butylarsine chloride,  $\text{C}_4\text{H}_9\cdot\text{AsPhCl}$ , is prepared from mercury *n*-dibutyl and phenylarsine chloride. It has b. p. 165–166°/14 mm.,  $d^{15}$  1.350. G. W. R.

**Is a New Structural Formula for Benzene Necessary?**

P. H. HERMANS (*Chem. Weekblad*, 1923, 20, 326—330).—From a survey of the various conceptions of valency and structure in organic compounds from the time of Kekulé onwards, it is concluded that attempts to formulate geometrical conceptions of valency and arrangement of atoms have now failed and must always fail to explain completely the mechanism of molecular structure. In spite of innumerable attempts to bring forward "structural formulæ" for benzene, the original conception of Kekulé alone satisfies our present knowledge, which is insufficient to elucidate the balance of forces within the benzene molecule. S. I. L.

**Direct Introduction of Substituents in the Benzene Nucleus.**

C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 244).—Those groups which require a hydrogen atom to give their most stable compounds induce substitution in the ortho- and para-positions, whilst groups which form their most stable compounds by addition of an hydroxyl group induce substitution to the meta-position. S. I. L.

**Direct Substitution in the Benzene Nucleus.**

P. G. VAN E. VLIET (*Chem. Weekblad*, 1923, 20, 279).—The fact that the hydroxyl group induces substitution in the meta-position is an obvious exception to Lely's rule (preceding abstract) that groups which form their most stable compounds by addition of one hydrogen atom induce substitution in the ortho- and para-positions. S. I. L.

**Lely's Substitution Rule.**

P. H. HERMANS (*Chem. Weekblad*, 1923, 20, 279—280).—Lely's rule (see preceding abstracts) is merely a less satisfactory form of Posner's, that a radicle induces substitution in the meta-position if its hydrogen compound cannot be directly oxidised to its hydroxyl compound. Lely's benzene formula is obtained by juggling with speculative hypotheses. S. I. L.

**The Substitution Rule of C. W. A. Lely.**

J. JÜRGENS (*Chem. Weekblad*, 1923, 20, 297).—Lely's rule leads to conclusions contrary to the experience of the directing influence of such groups as  $\text{OH}$ ,  $\text{COOR}$  ( $\text{R}$ =an alkyl group),  $\text{CONH}_2$ ,  $\text{CCl}_3$ , and  $\text{NH}_2$  in strongly acid solutions. Such rules serve rather to complicate than to clarify the problem (see preceding abstracts). S. I. L.

**The Substitution Rule.** C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 361—362).—A reply to Hermans and to Jürgens (preceding abstracts). The rule is said to apply only to simple cases, and exceptions where the directing group is complex are admitted. Obviously no rule can hold in all cases without a new structural formula for benzene. S. I. L.

**Kinetics of Catalytic Dehydrogenation.** N. ZELINSKY and PAVLOV (*Ber.*, 1923, 56, [B], 1249—1255).—The catalytic hydrogenation of cyclohexane to benzene and hydrogen in the

presence of platinised or palladised asbestos has been examined between the temperature limits  $151^{\circ}$  and  $408.5^{\circ}$ . The hydrocarbon is dropped at a uniform rate into an electrically heated tube containing the catalyst at the desired temperature, the liquid products of the reaction are condensed, and the evolved hydrogen is measured. The course of the change is deduced from the index of refraction of the liquid condensate or, preferably, from the volume of hydrogen. Platinised asbestos, prepared by soaking asbestos in concentrated chloroplatinic acid and formalin and precipitating the metal by means of sodium hydroxide, causes sensible dehydrogenation of cyclohexane at  $150^{\circ}$ , and the action becomes rapidly more marked as the temperature increases. Even at  $407^{\circ}$ , dehydrogenation does not appear to be accompanied by appreciable carbonisation of benzene or cyclohexane. Similar observations are recorded with palladised asbestos, the activity of which appears to be less than that of platinum. Deposition of carbon is not observed at any temperature below  $408^{\circ}$ . For some unexplained reason the efficiency of the catalyst diminishes somewhat after it has been once used, and then becomes constant. Metallic nickel is much less suitable as a dehydrogenating catalyst, since it acts much more slowly than platinum or palladium, and also causes side reactions such as the decomposition of cyclohexane into benzene and methane. The slight activity is attributed to the catalyst becoming coated with a thin layer of carbon, which diminishes its dehydrogenating power.

H. W.

**The Mechanism of the Pinacol-Pinacolin and Wagner-Meerwein Transformations.** CHRISTOPHER KELK INGOLD (T, 1923, 123, 1706—1713).

**The Volatilisation of Toluene in Steam.** JEAN BARBAUDY (*Compt. rend.*, 1923, 176, 1616—1618).—A study of the toluene-water system, pressure being constant at 760 mm., showed that the vapour was richer in water when the temperature rose above  $84.34^{\circ}$  than would be expected from a consideration of the relative vapour pressures of the two substances. The distillate on condensation yielded pure water, so that the conditions are represented by a point on the water condensation curve. On reducing the temperature to  $84.34^{\circ}$ , toluene appeared in the condensate and total condensation occurred. When the vapour contained less than 53.73% of water, pure toluene was the first liquid to be condensed and the conditions are, in the new case, represented by a point on the toluene condensation curve. Thus the equilibrium is represented by the two condensation curves and an ebullition line passing through their point of intersection, this last point being a true eutectic. This is in agreement with Dupré's vapour tension formula, which also holds when the vapour is saturated with respect to only one liquid. The last case is shown by the author to hold for the system investigated by determinations of the solubility of water in a mixture of toluene and water vapours, experimental details of which are given.

H. J. E.

**Unsaturation and Molecular Compound Formation. III.**

O. MAASS, E. H. BOOMER, and D. M. MORRISON (*J. Amer. Chem. Soc.*, 1923, 45, 1433—1438; cf. A., 1918, i, 534; 1921, i, 761).—The freezing points of the systems *o*-xylene, *p*-xylene, *m*-xylene, propylbenzene, and methylcyclohexane respectively with hydrogen bromide have been determined with molecular percentages of the hydrocarbon from one to one hundred. From the results it is shown that molecular compounds are formed with *m*-xylene and propylbenzene. The formation of molecular compounds is shown to be due to unsaturation. Failure to form a molecular compound in spite of unsaturation is due to the relatively great attraction of the hydrocarbon molecules for one another. J. F. S.

**Catalytic Action. II. Catalytic Preparation of *p*-Cymene and its Formation in Sulphite Turpentine.** SHIGERU KOMATSU, HISASHI NAKAMURA, and MASAO KURATA (*Mem. Coll. Sci. Kyoto*, 1923, 6, 183—186).—The turpentine obtained from spruce and other woods in the manufacture of pulp by the sulphite process consists mainly of *p*-cymene, not of terpenes. It is shown experimentally that pinene and menthene, but not menthol or borneol, can be dehydrogenated by heating with sulphur at 200° for twenty-four hours, forming *p*-cymene. It is suggested that *p*-cymene is formed in this manner from terpenes in the manufacturing process, since free sulphur is known to be present in the digester liquors. E. H. R.

**Influence of certain Substituents in the Benzene Nucleus on the Mobility of the Chlorine in a Side Chain, with Special Reference to the Problem of Substitution in the Benzene Nucleus.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1923, 42, 516—523; cf. A., 1922, i, 646).—In continuation of previous work, the author has examined the rates of hydrolysis in aqueous alcohol of substances of the type  $\text{CH}_2\text{Cl}-\text{C}_6\text{H}_4\text{X}$ , where X is either I or  $\text{CO}_2\text{H}$ . The rates were found to be in the order:  $\text{I}(p) > \text{I}(o) > \text{CO}_2\text{H}(m) > \text{I}(m) > \text{CO}_2\text{H}(p)$ . The materials used were prepared in the following manner: *p*-chloromethylbenzoic acid, m. p. 202.5—203° (literature 199° uncorr.), by hydrolysis of *p*-chloromethylbenzonitrile. *m*-Chloromethylbenzoic acid, m. p. 137.5—138.5° (literature 135°), from the nitrile, m. p. 67.4—67.8° (literature 67°). Attempts to prepare *o*-chloromethylbenzoic acid were unsuccessful. The *o*-, *m*-, and *p*-iodobenzyl chlorides were prepared from the corresponding iodotoluenes by bromination at 150—200°, the resultant iodobenzyl bromides were hydrolysed by refluxing with water, and the iodobenzyl alcohols so formed were treated with phosphorus pentachloride. *p*-Iodobenzyl bromide, m. p. 79.5—80° (literature 78.7°). *p*-Iodobenzyl alcohol, m. p. 72—73°; *p*-iodobenzyl chloride, m. p. 53—53.5° (described in the literature as a liquid). *m*-Iodobenzyl bromide, prisms, m. p. 50—50.5°, easily soluble in ether, chloroform, or carbon disulphide, moderately soluble in alcohol, insoluble in water. *m*-Iodobenzyl alcohol, b. p. 154°/10 mm. (literature gives 165°/16 mm.). *m*-Iodobenzyl chloride, crystals, m. p. 26.5—

27.5°. *o*-Iodobenzyl bromide, m. p. 55—55.5° (literature gives 52—53°). *o*-Iodobenzyl alcohol, needles, m. p. 89.5—90°. Easily soluble in ether or alcohol, sparingly soluble in hot water. *o*-Iodobenzyl chloride, m. p. 28.5—29.5°, easily soluble in organic solvents. Insoluble in water. F. A. M.

**Hydrogenation of *o*-Nitrostyrene.** A. GARCÍA BANÚS and J. PASCUAL VILA (*Anal. Fis. Quím.*, 1922, 20, 689—692).—The catalytic hydrogenation of *o*-nitrostyrene was attempted with the object of obtaining  $\beta$ -nitrophenylethane and, by reduction, the corresponding amino-compound. In ethereal solution, a grey precipitate is formed, which on recrystallisation gives white crystals, m. p. 237° (cf. Sonn and Schellenberg, A., 1918, i, 9). In ether-acetic acid solution, the oxime of phenylacetaldehyde, m. p. 95°, is obtained. An apparatus for the preparation of electrolytic hydrogen is described. G. W. R.

**Alkylation. I. The Preparation of Esters of Aromatic Sulphonic Acids.** V. A. IZMAILSKI and B. A. RAZORENOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 359—366).—The esters of aromatic sulphonic acids, which can be used as alkylating agents (see following abstract), are most conveniently prepared from the corresponding acid chlorides by the action of the relevant alcohol in the presence of aqueous 25% sodium hydroxide at a low temperature, the alkali being slowly added to the mixture of chloride and alcohol. The preparation of methyl and ethyl toluene-*p*-sulphonates is described, the yields being 92% and 85%, respectively. G. A. R. K.

**Alkylation. II. The Alkylation of the Nitrophenols.** V. A. IZMAILSKI and B. A. RAZORENOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 366—368).—The alkylation of the *o*- and *p*-nitrophenols is usually carried out by the action of alkyl halides on the dry sodium phenoxides, an operation necessitating the use of autoclaves and giving somewhat unsatisfactory yields of alkyl ethers. The action of methyl and ethyl toluene-*p*-sulphonates on the phenols in the presence of aqueous sodium hydroxide at 95—100° leads to a much more satisfactory result. Thus *o*-nitroanisole and *p*-nitrophenetole can be easily obtained in 90% yields by this method. G. A. R. K.

**Derivatives of Diphenyl. V. Nitrodiphenyls.** A. GARCÍA BANÚS and J. GUÍTERAS (*Anal. Fis. Quím.*, 1923, 21, 126—131).—By gentle nitration of 4-hydroxydiphenyl in acetic acid solution no mononitro-derivative is obtained, but only 3:5-dinitro-4-hydroxydiphenyl, m. p. 154—155°. More intense nitration gives 3:5:4'-trinitro-4-hydroxydiphenyl, m. p. 201—202°. Oxidation of the latter compound with chromic acid gives *p*-nitrobenzoic acid. G. W. R.

**Studies in Polymerisation. IX. The Polymerisation of *as*-Diphenylethylene.** S. V. LEBEDEV, I. A. ANDREYSKI, and A. A. MATTUSCHKINA (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 223—233).—It has been observed by Hildebrand (*Diss. Strassburg*,

1909) that on heating *as*-diphenylethylene with a trace of iodine a dimeric substance, m. p.  $112^{\circ}$ , was obtained which he considered to be 1:1:3:3-tetraphenylcyclobutane. It is now shown that by polymerisation of the hydrocarbon in the presence of sulphuric acid, or the silicate floridine, a mixture of two substances is found, namely, Hildebrand's compound (m. p.  $113.5^{\circ}$  when pure) and a new dimeric compound (m. p.  $143^{\circ}$ ). The first of these is shown to be  $\alpha\alpha\gamma\gamma$ -tetraphenyl- $\Delta^2$ -butylene,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CMePh}_2$ , for although it is very inert and is not attacked by permanganate, it gives a colour with tetranitromethane, forms a liquid *dibromide*, and an *ozonide*,  $\text{C}_{26}\text{H}_{24}\text{O}_8$ , which is a viscous, yellow liquid, yielding benzophenone,  $\alpha\alpha$ -diphenylpropaldehyde, and  $\alpha\alpha$ -diphenylpropionic acid by the action of water in addition to *benzophenone peroxide*, a microcrystalline compound insoluble in alcohol, decomposing into oxygen and benzophenone at about  $170^{\circ}$ . If the ozonisation of the compound, m. p.  $113.5^{\circ}$ , is very prolonged, some of the ozonide of *as*-diphenylethylene is also formed, which can be separated owing to its insolubility in light petroleum and gives benzophenone and formic acid on fission.

The dimeric compound, m. p.  $143^{\circ}$ , appears to be fully saturated in its behaviour towards ozone and bromine, and can be obtained by the isomerisation of the compound, m. p.  $113.5^{\circ}$ , by heating with floridine; it is suggested that it is 1:1:3:3-tetraphenylcyclobutane.  
G. A. R. K.

#### The Hydrogenation of Aromatic Compounds with the Aid of Platinum. VI. The Hydrogenation of Naphthalene.

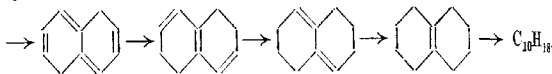
RICHARD WILLSTÄTTER and FRITZ SEITZ (*Ber.*, 1923, 56, [B], 1388—1407).—The hydrogenation of naphthalene in the presence of spongy platinum leads directly to the production of decahydronaphthalene (Willstätter and Hatt, A., 1912, i, 545; Willstätter and King, A., 1913, i, 353). Since this result appears at variance with the technical production of tetrahydronaphthalene, the problem has been again examined. Mixtures of naphthalene and its tetrahydro-derivative are treated with hydrogen, either pure or containing a small proportion of oxygen, in the presence of spongy platinum which is free from, moderately charged, or highly charged with oxygen.

Naphthalene is converted by hydrogen in the presence of spongy platinum rich in oxygen into tetrahydronaphthalene, whereas decahydronaphthalene is formed (without the production of a detectable intermediate product) if the catalyst is poor in oxygen. The primary formation of a dihydro-compound occurs in such manner that the hydrogen atoms become attached to one or to both of the benzene nuclei of naphthalene. Hydrogenation at one nucleus leads to a distinct break in the process (tetrahydronaphthalene) after which the addition continues much more slowly than with naphthalene itself. On the other hand, the addition of a hydrogen atom to each nucleus is followed by the production of a sequence of intermediate compounds each of which is less

saturated than naphthalene, and is hydrogenated at a much greater rate than the latter.

It appears very probable that the hydrogenation of naphthalene occurs in three distinct manners: (1) tetrahydronaphthalene is predominately produced when the oxygen content of catalyst and hydrogen is at a minimum; (2) the chief product is decahydronaphthalene when the oxygen content of platinum and hydrogen is low, and (3) tetrahydronaphthalene predominates when the oxygen content is considerable. The simplest explanation of these observations consists in the hypothesis that different dihydronaphthalenes are formed intermediately; three such substances are probably involved, one of which is the most stable and is capable of existence in the presence of a catalyst rich in oxygen, whereas another is so little stable towards spongy platinum that its formation is inhibited by the presence of even a small proportion of oxygen in the catalyst or hydrogen.

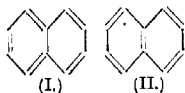
Hydrogenation occurring in both nuclei can lead through 1:5-di-hydronaphthalene to the following intermediate products:



Incidental observations by Bamberger and his co-workers appear to show that the products of the hydrogenation of naphthalene by sodium and ethyl or amyl alcohols contain components in which the hydrogen is present in both nuclei.

$\Delta^2$ - and  $\Delta^1$ -Dihydronaphthalenes are the only primary products of the hydrogenation of naphthalene at a single benzene nucleus which require to be considered. The former of these probably loses its hydrogen more readily, and is therefore the less stable towards spongy platinum rich in oxygen. The  $\Delta^1$  compound is the more stable and is the probable intermediate product in the formation of tetrahydronaphthalene in the presence of platinum rich in oxygen.

The author reaffirms his contention (cf. Willstätter and King, *loc. cit.*) that it is impossible to explain the peculiarities of the behaviour of naphthalene by a single structural formula. The unsymmetrical structure, (I) explains the production of derivatives hydrogenated in only one benzene nucleus, whereas the symmetrical configuration (II) is in accordance with the production of binuclear hydro-derivatives.



The hydrogenation of naphthalene is not catalysed by very finely divided platinum which is free from oxygen. Spongy platinum, poor and richer in oxygen, catalytically accelerates the hydrogenation; the action of the metal is different under the different conditions. A more rigid discrimination is necessary between specimens of spongy platinum containing, respectively, the minimum necessary amount, small quantities, and larger proportions of oxygen.

Spongy platinum saturated with oxygen appears to induce hydrogenation through the most stable intermediate products, whereas that poorer in oxygen causes the change to occur through intermediate phases of smaller stability.

H. W.

**The Series of the Methylnaphthalenes.** FRITZ MAYER and OTTO SCHNECKO (*Ber.*, 1923, 56, [B], 1408—1415).—An extension of previous work (*A.*, 1922, i, 740).

*2-Iodo-1-methylnaphthalene*, colourless leaflets, m. p. 53°, b. p. 196—199°/30 mm., is prepared from 1-methyl- $\beta$ -naphthylamine by diazotisation and treatment of the product with potassium oxide. It is converted by successive treatment with magnesium and carbon dioxide into 1-methyl-2-naphthoic acid, colourless needles, n. p. 178° (ethyl ester, colourless crystals, m. p. 27—28°, b. p. 190°/20 mm.), which, like the isomeric 2-methyl-1-naphthoic acid (*loc. cit.*) could not be oxidised to the corresponding dicarboxylic acid; 1:1'-dimethyl-2:2'-dinaphthyl, colourless needles, n. p. 227°, is obtained as a by-product of the preparation of the acid.

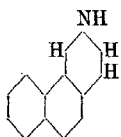
6-Amino-5-methyl-1:2:3:4-tetrahydronaphthalene, a colourless liquid which does not absorb carbon dioxide from the air and can be diazotised and coupled with  $\beta$ -naphthol, b. p. 170—175°/30 mm., is prepared by reducing 1-methyl- $\beta$ -naphthylamine with sodium and amyl alcohol; the corresponding acetyl derivative, lustrous leaflets, m. p. 134°; the benzoyl derivative, m. p. 222°, and the hydrochloride, colourless needles, m. p. 263—264°, are described.

Dinaphtholmethane is converted by ammonium sulphite and ammonia at 150—160° into 1:2:1':2'-dinaphthacridine, straw-yellow needles, m. p. 216°, whereas at 110—120° 2-amino-2'-hydroxy-1:1'-naphthylmethane, lustrous leaflets, m. p. 121°, is produced the corresponding acetyl derivative, lustrous leaflets, m. p. 132°, and the benzoyl compound, colourless needles, m. p. 159°, are described).

Ethyl 2- $\beta$ -naphthylpropionate, colourless leaflets, m. p. 28°, b. p. 95—98°/25 mm., is converted by hydrazine hydrate in boiling alcoholic solution into the corresponding hydrazide, slender needles, m. p. 156°, which is transformed successively into the unstable diurethane, colourless leaflets, m. p. 83°, and 2- $\beta$ -naphthyl-ethylamine, b. p. 174—175°/25 mm. (benzoyl derivative, rhombic crystals, m. p. 140—141°; picrate, long, yellow needles, m. p. 196°). Alternatively, the amine is produced by converting  $\beta$ -naphthyl-ethyl bromide into the corresponding cyanide, m. p. 86°, b. p. 12—205°/28 mm., and reducing the latter under pressure with hydrogen in the presence of nickel as catalyst and tetrahydronaphthalene as solvent; the primary base is thereby obtained in 10% yield together with di-2- $\beta$ -naphthylethylamine, colourless needles, m. p. 87° (nitroso-derivative, lustrous leaflets, m. p. 179°; picrate, yellow needles, m. p. 138—139°; hydrochloride, lustrous leaflets, m. p. 289°).  $\alpha$ -Naphthylmethyl cyanide is similarly hydrogenated to a mixture of  $\beta$ -1-naphthylethylamine, a colourless liquid, b. p.

182—183°/18 mm. (*picrate*, yellow needles, m. p. 201—202°; *benzoyl* derivative, colourless needles, m. p. 97° after softening at 87°), and *di-β-1-naphthylethylamine*, a colourless, viscous liquid, b. p. above 320°/200 mm. (*picrate*, lustrous leaflets, m. p. 179°; *nitroso*-derivative, lustrous leaflets, m. p. 114—115°; *hydrochloride*, m. p. 222°). The course of the hydrogenation depends greatly on the purity of the  $\alpha$ -naphthylmethyl cyanide; traces of admixed bromo-compounds inhibit the change.

$\beta$ -2-Naphthylethylamine condenses with methylal to give 1:2:3:4-tetrahydronaphthaisoquinoline, b. p. 200—205°/20 mm., m. p. 40°, in poor yield. With formaldehyde in the presence of ether it slowly gives the compound  $C_{16}H_{17} \cdot CH_2 \cdot CH_2 \cdot N \cdot CH_3$ , needles, m. p. 117°, in 80 % yield. The latter substance is converted by warm,



concentrated hydrochloric acid into naphthate-tetrahydroisoquinoline (annexed formula); the *picrate* needles, m. p. 225—226°; the *dihydrocarbamate*  $C_{27}H_{26}N_2S_2$ , m. p. 192° after previous darkening the *nitrosoamine*, lustrous leaflets, m. p. 105°; the *hydrochloride*, colourless needles, m. p. 275—276°; the *carbonate*, a white powder, incipient decomposition at 124°, and the *o*-nitrobenzoyl derivative, m. p. 240°, after previous darkening, are described. The base is oxidised by successive treatment with potassium permanganate and nitric acid to benzene 1:2:3:4-tetracarboxylic acid, m. p. 238°. Attempts to obtain a quinoline derivative from  $\beta$ -1-naphthylethylamine were unsuccessful by reason of the tendency for ring closure to occur in the peri-position. H. W.

#### Equations for Vapour Pressures and Latent Heats of Vaporisation of Naphthalene, Anthracene, Phenanthrene, and Anthraquinone. O. A. NELSON and C. E. SENSEMAN (*Ind. Eng. Chem.*, 1923, 15, 621—622).—The observed vapour pressures

of the above are in close agreement with the values calculated from the Clapeyron equation of state,  $dP/dT = L/(V - v)T$  (1). Approximating, this equation may be written  $dP/dT = L/(RT^2/P)$  (2), which

gives  $L = (\log P_2 - \log P_1) T_1 T_2 \left( \frac{2.303 R}{T_2 - T_1} \right)$  (3). By plotting the calculated decrease in  $L$  against increase in temperature or pressure the equation for  $L$  is obtained. Whilst  $L$  decreases appreciably in the first three cases, with anthraquinone only a slight decrease is observed. In each case,  $L$  could be represented, over the temperatures and pressures studied, by a linear equation,  $L = a + bT$ , although this linear function only holds for short temperature intervals. Substituting in (2), the Clapeyron equation becomes

$\log P = C - \frac{a}{4.5795 T} - \frac{b}{1.9875} \log T$ . Calculations of the entropy of vaporisation,  $L/RT$  (cf. Hildebrand, *J. Amer. Chem. Soc.*, 1915, 37, 970) give values in the neighbourhood of 13.7, whence it is concluded that the above compounds all form normal liquids.

W. T. K. B.

**Preparation of 9-Anthracyl Sulphide and 9-Anthracyl-mercaptan.** PETRI & STARK, G. M. B. H. (D.R.-P. 360608; from *Chem. Zentr.*, 1923, ii, 481).—Anthracene is treated with sulphur monochloride in the presence of a catalyst with or without a solvent or diluent, according as the temperature of reaction is about 100° or the ordinary temperature, respectively. The product of reaction is treated with a reducing agent. For example, anthracene is heated with sulphur monochloride with the addition of benzene in the presence or absence of zinc dust, aluminium, or aluminium chloride, until evolution of hydrogen chloride ceases. After removal of benzene by distillation, the product is heated at 130° with hydrous sodium sulphide, whereby the sodium salt of 9-anthracyl mercaptan is obtained as light yellow leaflets. Treatment of the sodium salt with acid yields 9-anthracyl mercaptan,  $C_{14}H_9SH$ . It forms yellow prisms and gives by mild oxidation 9-anthracyl sulphide, lustrous, orange-yellow prisms, m. p. 220–221°. The methyl ether of anthracyl mercaptan,  $C_{14}H_9SMe$ , forms yellow needles, m. p. 157°. By oxidation with strong oxidising agents such as chromic oxide, these compounds yield anthraquinone.

G. W. R.

**Certain Bromo-derivatives of Acenaphthene.** REMO DE FAZI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 343–345).—Replacement by chloroform of the ether used as solvent in Graebe and Guinibourg's method for preparing 4-bromoacenaphthene (A., 1903, i, 408) results in the formation of a certain proportion of tetrabromoacenaphthene (cf. Ewan and Cohen, T., 1889, 55, 578). Oxidation of 4-bromoacenaphthene yields 4-bromonaphthalene-1 : 8-dicarboxylic acid, m. p. 220–221°, and 4-bromoacenaphthenequinone, m. p. 236.5–237°; the melting points given in the literature for these compounds are, respectively, 210° and 194°.

T. H. P.

**Substitution in Acenaphthene. I. The Sulphonation of Acenaphthene.** K. DZIEWOŃSKI and T. STOŁYKHO (*12ty Zjazd Chemików Polskich*, 1923, 57).—The sulphonation of acenaphthene leads to the production of two isomeric monosulphonic acids and of four isomeric disulphonic acids. The oxidation of these products shows that substitution has occurred in the naphthalene nucleus, contrary to the generally accepted view. The monosulphonic acids, however, on distillation with potassium cyanide yield a product in which the sulphonic group is substituted in the side ring.

R. T.

**Substitution in Acenaphthene. II. The Bromo-nitro-, Bromo-sulphono-, and Nitro-sulphono-derivatives of Acenaphthene.** K. DZIEWOŃSKI, (Mlle) A. GLASNERÓWNA, and T. ORZELSKI (*12ty Zjazd Chemików Polskich*, 1923, 57).—Substitution in  $\alpha$ -nitroacenaphthene is extremely difficult, the  $\alpha$ -nitro-sulphonic or halogen derivatives being prepared by the nitration of halogen substituted acenaphthenes, or of the acenaphthenesulphonic acids. The products thus obtained exhibit great chemical activity, and mobility of the substituents.  $\alpha$ -Bromoacenaphthene is easily converted into  $\alpha$ -bromoacenaphthenedisulphonic acid.

R. T.

**The Polymerisation of Acenaphthylene. I. Polyacenaphthylene and Allopolyacenaphthylene.** K. DZIEWOŃSKI and (MLLE) J. OLESIÓWNA (*1<sup>st</sup> Zjazd Chemików Polskich*, 1923, 58).—Acenaphthylene is converted by strong acids into *polyacenaphthylene*,  $(C_{12}H_8)_{22}$ , and *allopolyacenaphthylene*  $(C_{12}H_8)_8$ . Polyacenaphthylene is converted by bromination into *bromopolyacenaphthylene*,  $C_{264}H_{144}Br_{221}$ .  
R. T.

**The Nitration of 1:1'-Dinaphthyl.** C. S. SCHOEFFLE (*J. Amer. Chem. Soc.*, 1923, 45, 1566—1571).—It is shown that  $\beta$ -dinaphthol, when distilled with zinc dust, gives  $\beta$ -dinaphthylene oxide and not 1:1'-dinaphthyl as stated by Walder (A., 1883, 208). Consequently the compounds described as mono- and di-nitro-1:1'-dinaphthyl (Julius, A., 1887, 56) are mono- and di-nitro- $\beta$ -naphthylene oxide, respectively.

1-Iodonaphthalene, from which Ullmann and Bielecki (A., 1901, i, 586) prepared 1:1'-dinaphthyl by the action of copper powder at 285°, is not readily obtainable, but 1-bromonaphthalene may be used, the yield of dinaphthyl being satisfactory if the reaction is conducted at 280—285° in the presence of a small amount of iodine. Small quantities of 1:2-dinaphthyl, 2:2'-dinaphthyl, perylene, and a compound, m. p. 282—283°, probably dinaphthyl-naphthalene (Weitzenböck and Seer, A., 1913, i, 847), are also produced.

The nitration of 1:1'-dinaphthyl in acetic acid solution at 90—95° gives an 85% yield of 4-nitro-1:1'-dinaphthyl, pale yellow needles, m. p. 104°; the further nitration of this compound, which need not be isolated, gives 4:4'-dinitro-1:1'-dinaphthyl, pale yellow crystals, m. p. 246°, in 60% yield, together with small amounts of two isomeric dinitro-derivatives, which melt at 144° and 228°, respectively. The structures of 4-nitro-1:1'-dinaphthyl and 4:4'-dinitro-1:1'-dinaphthyl have been verified by synthesising the latter, by the action of copper powder at 220—230° on 4-nitro-1-iodonaphthalene.  
W. S. N.

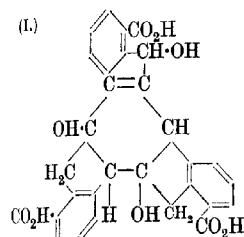
**Decacyclene. I. The Reduction of Decacyclene.** K. DZIEWOŃSKI and J. SUSZKO (*1<sup>st</sup> Zjazd Chemików Polskich*, 1923, 55; cf. A., 1903, i, 431).—Decacyclene (trinaphthalenebenzene) is reduced by means of hydriodic acid and red phosphorus, at 270—290° under pressure. A series of reduction products is obtained having the composition  $C_{36}H_{24}$ ,  $C_{36}H_{26}$ ,  $C_{36}H_{30}$ ,  $C_{36}H_{34}$ ,  $C_{36}H_{36}$  and  $C_{36}H_{40}$ . In all these the benzene nucleus remains unattacked, showing that the benzene ring in compounds of this type is much more stable than in free benzene.  
R. T.

**Decacyclene. II. The Oxidation and Degradation of Decacyclene.** K. DZIEWOŃSKI, (MLLE) J. ŁAZOWSKA, and D. WANDYCZ (*1<sup>st</sup> Zjazd Chemików Polskich*, 1923, 55—56; cf. A., 1913, i, 848).—Decacyclene is oxidised by means of chromic acid, and the product shown to be a mixture of two keto-acids  $(C_{12}H_8O_2)_2$  or  $(C_{12}H_8O_4)_2$ , and  $(C_{10}H_6O_4)_2$ . The first of these acids is the primary oxidation product, as on oxidation it yields the second acid, which on further oxidation yields a truxene derivative, and finally a benzenetricarboxylic acid.  
R. T.

**Decacyclene. III. The Sulphonation of Decacyclene.** K. DZIEWOŃSKI and J. POCHWAŃSKI (*12<sup>ty</sup> Zjazd Chemików Polskich*, 1923, 56).—The action of concentrated sulphuric acid on decacyclene is to produce *decacyclenetrisulphonic acid*,  $C_{36}H_{15}(SO_3H)_3$ , a yellow acid dye, which on oxidation is converted into various coloured substances of a phenolic or quinonoid nature, and finally into the two keto-acids obtained by the direct oxidation of decacyclene.

R. T.

**Degradation of Decacyclene [Trinaphthylenebenzene].** K. DZIEWOŃSKI and J. PODGÓRSKA (*Bull. Acad. Sci. Cracow*, 1915; from *Chem. Zentr.*, 1923, i, 525–526; cf. A., 1913, i, 848).—Trimethyl tribenzoylbenzenetricarboxylate (*truxenquinonetricarboxylate*) forms yellow needles,

calcium hydroxide, *truxenol*,

by elimination of carbon dioxide. It forms satin-like needles, m. p.

338–340°. By reduction, *truxene*,  $C_6(\begin{smallmatrix} CH_2 \\ | \\ C_6H_4 \end{smallmatrix})_3$ , is formed; light

yellow needles or tablets, m. p. 364–365°. The hydrocarbon dissolves in sulphuric acid containing a trace of nitric acid.

G. W. R.

**Picrates of some Tertiary Amines.** SHIGERU KOMATSU and UMESABURO TAKIMOTO (*Mem. Coll. Sci. Kyoto*, 1923, 6, 173–176).—The melting points of the picrates of some aromatic tertiary amines determined by Komatsu (A., 1913, i, 39) have been criticised by Singh (T., 1916, 109, 789). Some of these have now been redetermined, and slightly higher values have been found, although not so high as those found by Singh. The new values given are dimethylaniline picrate, 158–159.5°; diethylaniline picrate, 137–138°; methylethylaniline picrate, 127–128.3°. E. H. R.

**Catalytic Decomposition of Anilides.** A. MAILHE (*Compt. rend.*, 1923, 176, 1716–1719).—The catalytic decomposition of the anilides of acetic, propionic acid, etc., occurs along the same lines as that of formanilide (this vol., i, 458), the secondary amine produced by the loss of carbon monoxide being further decomposed into primary amine and aliphatic hydrocarbon. Subsidiary reactions result in the formation of carbon dioxide, hydrogen, methane, and small amounts of ammonia and carbon. No catalyst

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could be found by means of which the formation of the secondary amine could be catalysed and its subsequent decomposition suppressed, although both precipitated copper and alumina were tried instead of nickel.

G. F. M.

**$\beta$ -Nitroarylhydroxylamines.** I.  $\beta$ -2:4- and  $\beta$ -2:6-Dinitrophenylhydroxylamine. W. BORSCHÉ (*Ber.*, 1923, 56, [B], 1494—1501).—The unexpected reactivity of 2:4-dinitroanisole and 2:4-dinitrodiphenyl ether (Borsche, this vol., i, 780) has led the authors to examine the behaviour of these and associated substances towards hydroxylamine. A series of  $\beta$ -nitrophenylhydroxylamines which are otherwise very difficultly accessible has thereby been obtained.

$\beta$ -2:4-Dinitrophenylhydroxylamine, leaflets or flattened needles, m. p. about  $80^\circ$  (decomp.), according to the rate of heating, is prepared by heating 2:4-dinitroanisole or 2:4-dinitrodiphenyl ether with hydroxylamine in alcoholic solution. The substance is stable when dry, but decomposes very readily in solution with evolution of nitric oxide and formation of dark red or brownish-black resins; the solutions can be stabilised in certain cases by the addition of salts of hydroxylamine.  $\beta$ -2:4-Dinitrophenylhydroxylamine has pronouncedly acidic properties; the sodium and barium salts, the ammonium compound,  $C_6H_3O_5N_3 \cdot NH_4$ ,  $C_6H_3O_5N_3$ , black needles with a green reflex, m. p.  $142^\circ$  (decomp.), and the aniline compound,  $C_6H_3O_5N_3 \cdot NH_2Ph$ , dark-red plates, m. p.  $111$ – $112^\circ$  (decomp.), are described. It is reduced by ammonium sulphide to 4-nitro-*o*-phenylenediamine. It is oxidised by chromic acid in the presence of glacial acetic acid to 1:3-dinitro-4-nitrosobenzene, dark yellow needles, m. p.  $133^\circ$ , to a dark green liquid, and by fuming nitric acid (*d* 1.54) to 1:2:4-trinitrobenzene, m. p.  $60^\circ$ . *O*-Acetyl- $\beta$ -2:4-dinitrophenylhydroxylamine, lustrous, yellow needles, m. p.  $164^\circ$  (decomp.), after previous darkening and softening, is prepared by the action of acetic anhydride on  $\beta$ -2:4-dinitrophenylhydroxylamine at the atmospheric temperature. In contrast to the parent substance, it is relatively stable towards boiling acetic anhydride, by which it is converted into diacetyl- $\beta$ -2:4-dinitrophenylhydroxylamine,  $C_{10}H_9O_7N_3$ , pale yellow leaflets, m. p.  $141^\circ$ , and much resinous matter. *O*-Benzoyl- $\beta$ -2:4-dinitrophenylhydroxylamine, obtained by the aid of benzoyl chloride in the presence of pyridine, crystallises in long, dark yellow needles, m. p.  $163$ – $164^\circ$  (slow decomp.).  $\beta$ -2:4-Dinitrophenylhydroxylamine methyl ether, dark-yellow, acute prisms, m. p.  $110$ – $111^\circ$ , is prepared by the action of methyl sulphate and sodium hydroxide on the hydroxylamine. It is reduced by ammonium sulphide to 4-nitro-*o*-phenylenediamine. It is converted by diazomethane in the presence of ether into the dimethyl compound,  $C_8H_9O_5N_3$ , pale yellow needles, m. p.  $87^\circ$ .  $\beta$ -Benzoyl- $\beta$ -2:4-dinitrophenylhydroxylamine methyl ether crystallises in pale yellow needles, m. p.  $155^\circ$ .

$\beta$ -2:6-Dinitrophenylhydroxylamine, coarse needles, m. p.  $115^\circ$  (decomp.), is prepared in 81% yield from 2:6-dinitrodiphenyl ether; it is less stable in substance, more stable in solution, than the

someric 2:4-dinitro-compound. *Dibenzoyl-β-2:6-dinitrodiphenylhydroxylamine* crystallises in pale yellow, lustrous prisms, m. p. 168–169°. The hydroxylamine is oxidised by fuming nitric acid (1.54) to 1:2:3-trinitrobenzene, long, pale yellow needles, m. p. 121°. H. W.

**Preparation of Pure Dehydrothiotoluidine.** R. F. HUNTER (*J. Soc. Chem. Ind.*, 1923, 42, 302r.).—A description of a laboratory preparation of dehydrothio-*p*-toluidine by heating *p*-toluidine and sulphur. A maximum yield amounting to 30% of theory was obtained, m. p. 191°. [According to Paul, *Z. angew. Chem.*, 1896, 9, 681; *J. Soc. Chem. Ind.*, 1897, 730; and Casseller, D.R.-P. 53938, yields of 50% to 75% of theory are readily obtainable by using naphthalene as a solvent.] F. A. M.

**Destructive Action of Nitric Acid on Phenols.** MOTONO (WATA) (*J. Chem. Soc. Japan*, 1923, 44, 391–406).—If 60% nitric acid is dropped gradually on gallic acid, and, when reaction has ceased, the mixture heated on a water-bath, the gallic acid (1 mol.) is almost completely decomposed into carbon dioxide, hydrocyanic acid, oxalic acid (nearly 1 mol.), and water; acetic acid could not be detected. The hydrocyanic acid is regarded as a by-product, the amount being only 1–2%. For the production of oxalic acid the concentration of the nitric acid (30–60%) has scarcely any effect. Using the production of hydrocyanic and oxalic acids as a test, the decomposing action of nitric acid on phenols and carboxylic acids has been examined; the percentages given below are those of nitric acid at the lower limit for the decomposition at the ordinary temperature (*a*) and on heating (100°) (*b*) respectively: gallic acid, *a* 30%, *b* 8%; protocatechuic acid, *a* 30%, *b* 1.5–2%; salicylic acid, *a* no action, *b* 8.1%; pyrogallol, *a* 30%, *b* 20%; phloroglucinol, *a* no action, *b* 15% (no decomposition by 8% acid); resorcinol, *a* no action, *b* 15%; quinol, *a* 30%, *b* 15% (no decomposition by 8% acid); guaiacol, *a* 30%, *b* 8% (no decomposition by 6% acid); phenol, *a* 50% accompanied by nitration, *b* 8.1–11%; thymol, *a* and *b* concentrated acid; benzoic acid, *a* and *b* no decomposition by concentrated acid; toluene, benzene, and naphthalene, *a* and *b* no decomposition; gallotannin, *a* concentrated acid, *b* 30%. With *α*- and *β*-naphthols, hydrocyanic acid is produced on warming, but no oxalic acid. The entrance of hydroxyl and carboxyl groups into the benzene nucleus promotes the decomposition. K. K.

**2-Phenylcyclohexanol and 2-Bromocyclohexanol.** PIERRE BÉDOS (*Compt. rend.*, 1923, 177, 111–113; cf. A., 1922, i, 334, and this vol., i, 101).—Magnesium phenyl bromide converts cyclohexene oxide into 2-phenylcyclohexanol and, as secondary product, cyclohexenol, C<sub>6</sub>H<sub>10</sub>O. The former alcohol is a colourless liquid, b. p. 138–140°/11 mm., *d*<sub>4</sub><sup>16</sup> 1.035, *n*<sub>D</sub><sup>16</sup> 1.5415, phenylurethane, b. p. 135–136°, and hydrogen phthalate, m. p. 185–186°. When distilled with potassium hydrogen sulphate it gives a phenylcyclohexene, b. p. 125–126°/17 mm., *d*<sub>4</sub><sup>14</sup> 0.982, and *n*<sub>D</sub><sup>14</sup> 1.5505. The cyclohexenol has b. p. 65°/7 mm., *d*<sub>20</sub><sup>20</sup> 1.0, and *n*<sub>D</sub><sup>20</sup> 1.499; the phenyl-  
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urethane, m. p. 107—108°, is identical with that obtained by Brunel (*Thesis*, Paris, 1905) from a cyclohexenol obtained from a different source.

The above phenylcyclohexanol is probably a stereoisomeride of that (m. p. 54—55°, phenylurethane, m. p. 138—139°) obtained by Braun, Grüber, and Kirschbaum (this vol., i, 107). The hexanol melting at 54—55° has been obtained by reducing 2-phenylcyclohexanone (Le Brazidic, A., 1915, i, 12) with sodium and alcohol.

2-Bromocyclohexanol is obtained by the action of water on the intermediate Grignard additive compound (above) (cf. Blaise, A., 1902, i, 357). It is a colourless liquid, b. p. 87—88°/9 mm.,  $d_4^{25}$  1.402,  $n_D^{25}$  1.528; phenylurethane, m. p. 87—88°. E. E. T.

**The Decomposition of Ethers by Metallic Sodium.** J. F. DURAND (*Bull. Soc. chim.*, 1923, [iv], 33, 734—735; cf. this vol., i, 207, and A., 1921, i, 89).—A claim for priority against Schörigin. H. H.

**The Exchange of the Group ·OR in Nitrophenyl Ethers by other Radicles.** W. BORSCHKE (*Ber.*, 1923, 56, [B], 1488—1493).—The action of ammonia, aniline, hydrazine, phenylhydrazine, and ethyl sodioacetate on a number of nitrophenyl ethers has been investigated under comparable conditions. It is found that the hydrazino-group is most readily introduced into the benzene nucleus in place of the group ·OR and that the phenyl ethers of the nitrated phenols are more reactive than the alkyl ethers.

A full description is given of the preparation of 2:4-dinitroanisole, 2:4-dinitrodiphenyl ether, 3:5-dinitro-*o*-tolylmethyl ether, 3:5-dinitro-*p*-tolylmethyl ether, 3-nitroanisonitrile, ethyl 3-nitroanisate, 3-nitro-4-phenoxybenzonitrile, acute, pale yellow prisms, m. p. 79°, and ethyl 3-nitro-4-phenoxybenzoate, pale yellow, coarse crystals, m. p. 93—94°.

2:4-Dinitroanisole is converted by ammonia in aqueous alcoholic solution at 40—50° to a small extent into dinitroaniline which, under analogous conditions, is formed in good yield from 2:4-dinitrodiphenyl ether.

2:4-Dinitrodiphenylamine, m. p. 155—156°, is formed from the corresponding phenyl ether and aniline at 180°, whereas 2:4-dinitroanisole is converted into smeary products; 3:5-dinitro-*o*- and -*p*-tolyl methyl ethers are only partly changed, whereas 3-nitro-4-phenoxybenzonitrile is almost unaffected.

The following compounds are obtained by the use of hydrazine: 2:4-dinitrophenylhydrazine, m. p. 197—198° (decomp.); 6-nitro-1-hydroxy-4-methyl-1:2:3-benzotriazole,  $\text{NO}_2\text{C}_6\text{H}_4\text{Me} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N}(\text{OH}) \end{smallmatrix} \text{N}$ , pale yellow leaflets, m. p. 225° (decomp.), and the corresponding hydrazine salt, small, yellow needles, from 3:5-dinitro-*o*-tolyl methyl ether; 4-nitro-6-methyl-1:2:3-benzotriazole, slender, pale yellow needles, m. p. 241° (decomp.), from 3:5-dinitro-*p*-tolyl methyl ether; 3-nitro-4-hydrazinobenzonitrile, m. p. 221—222°, from 3-nitroanisonitrile or 3-nitro-4-phenoxybenzonitrile; ethyl 3-nitro-

4-hydrazinobenzoate, yellow needles, m. p.  $103^{\circ}$ , from ethyl 3-nitroanisate or ethyl 3-nitro-4-phenoxybenzoate; 1:2:3-benztriazole, n. p. (hydrated)  $104^{\circ}$  (decomp.), followed by resolidification and fusion at  $157-158^{\circ}$ , m. p. (anhydrous)  $157-158^{\circ}$ , from *o*-nitroanisole or *o*-nitrodiphenyl ether; under similar conditions, *p*-nitroanisole remains unchanged.

2:4-Dinitrodiphenyl ether is converted by phenylhydrazine in boiling alcoholic solution into 5-nitro-2-phenyl-2:1:3-benztriazole,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{N} \\ \diagup \diagdown \end{smallmatrix} \text{NPh}$ , m. p.  $176-178^{\circ}$ , whereas under like con-

ditions 2:4-dinitroanisole is almost unaffected, 3:5-Dinitro-*o*-tolyl methyl ether is transformed similarly into 5-nitro-2-phenyl-2-methyl-2:1:3-benztriazole, brownish-yellow needles, m. p.  $164^{\circ}$ . 3:5-Dinitro-*p*-tolyl methyl ether, 3-nitroanisonitrile, and 3-nitro-phenoxybenzonitrile do not react with an equivalent amount of boiling phenylhydrazine.

2:4-Dinitroanisole and 2:4-dinitrodiphenyl ether are transformed by ethyl sodioacetoacetate in the presence of alcohol and enzyme into ethyl  $\alpha$ -2:4-dinitrophenylacetoacetate, coarse yellow needles, m. p.  $97-98^{\circ}$ . 3:5-Dinitro-*o*-tolyl methyl ether does not react with ethyl sodioacetoacetate under similar conditions.

H. W.

**Improved Preparation of Thymol.** HOWARD & SONS, LTD., and J. W. BLAGDEN (Brit. Pat. 1923, 197848).—By condensing isopropyl alcohol at  $90^{\circ}$  with polysulphonated *m*-cresol in presence of sulphuric acid, polysulphonated thymol is obtained in satisfactory yield. The sulphonic acid groups are eliminated from the product by treatment with superheated steam.

T. S. W.

**Synthesis of Thymol from *p*-Cymene.** I. MAX PHILLIPS and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, 12, 733-734).—*p*-Cymene is isolated from a crude oil obtained from a sulphite pulping mill. After purification, it is nitrated, and the nitro-*p*-cymene reduced to cymidine by means of iron powder and hydrochloric acid. Sulphonation of cymidine gives a mixture of *o*- and *p*-cymidinesulphonic acids, which, by diazotisation and subsequent treatment with ethyl alcohol and copper powder, are successively converted into the corresponding diazocymenesulphonic acids and the same *p*-cymene-3-sulphonic acid, the sodium salt of which yields thymol on fusion with sodium hydroxide (cf. following abstract).

W. S. N.

**Synthesis of Thymol from *p*-Cymene.** II. MAX PHILLIPS (*Amer. Chem. Soc.*, 1923, 45, 1489-1493).—The synthesis of thymol from *p*-cymene (cf. preceding abstract) has been modified and improved. Conditions of working are given by which nitro-*p*-cymene may be reduced to cymidine, by means of iron powder and hydrochloric acid, in 80-85% yield, and a process is described by which cymidine may be sulphonated, giving an 80% yield of cymidinesulphonic acid. A new method for the elimination of the amino-group is adopted. Cymidinesulphonic acid is diazotised,

and the diazocymenesulphonic acid collected and treated with cold aqueous sodium hydrogen sulphite. After one hour the orange-coloured solution is heated to boiling and treated with hydrochloric acid. On concentration, *cymethydrazine-p-sulphonic acid*, m. p.  $260^{\circ}$  (decomp.), is obtained in 70–75% yield. It forms a *barium* salt, pale yellow plates. The hydrazinesulphonic acid is treated in boiling aqueous solution with an excess of copper sulphate, and the resulting cymene-*p*-sulphonic acid isolated as its sodium salt. For the production of thymol by the fusion of this salt with alkali, potassium hydroxide is far superior to sodium hydroxide. The best yield (59%) is obtained using three parts of potassium hydroxide to one part of sulphonate at  $350^{\circ}$ , with a fusion period of thirty minutes.

W. S. N.

**Catalytic Action. I. Catalytic Reduction of  $\alpha$ -Naphthol and  $\alpha$ -Naphthylamine.** SHIGERU KOMATSU and RYUZABURO NODZU (*Mem. Coll. Sci. Kyoto*, 1923, 6, 177–181).—When  $\alpha$ -naphthol was passed with pure hydrogen over reduced nickel at  $100$ – $110^{\circ}$ , a yield of about 41% of crude *ar*-tetrahydro- $\alpha$ -naphthol was obtained, together with 51% of  $\alpha$ -ketotetrahydronaphthalene containing some tetrahydronaphthalene. At  $135$ – $145^{\circ}$ , only 10% of the *ar*-compound was obtained and 90% of mixed *ac*-compound and hydrocarbon. When  $\alpha$ -naphthylamine was reduced in a similar manner at  $135$ – $145^{\circ}$ , 90% was converted into *ar*-tetrahydro- $\alpha$ -naphthylamine, the remainder being tetrahydronaphthalene formed from *ac*-tetrahydro- $\alpha$ -naphthylamine. E. H. R.

**Dinitrosoresorcinol.** W. R. ORNDORFF and M. L. NICHOL (*J. Amer. Chem. Soc.*, 1923, 45, 1536–1539).—Dinitrosoresorcinol when dried to constant weight under reduced pressure over sulphuric acid, contains one molecule of water of crystallisation, and decomposes at  $162$ – $163^{\circ}$  (cf. Morgan and Moss, T., 1922, 121, 2861; Bülow, A., 1904, i, 609). It forms thin, rhombic plates [*a* : *b* : *c* = 0.9 (?) : 1 : 0.613].

W. S. N.

**The Bromination of Organic Compounds.** K. W. ROSEMMUND and W. KUHNHENN (*Ber.*, 1923, 56, [B], 1262–1269).—Difficulties are not infrequently encountered in the bromination of aliphatic and aromatic compounds by reason of the impossibility of limiting the action in the desired manner. As mild brominating agents, pyridine and quinoline dibromide hydrobromides (particularly the former) are found to be very useful reagents, the reaction being usually effected in a glacial acetic acid solution. A very convenient modification of the method consists in dissolving the substance to be brominated and pyridine or quinoline hydrochloride or hydrogen sulphate in glacial acetic acid and adding the calculated amount of bromine solution from a burette; with colourless or faintly coloured substances, the termination of the reaction is fairly sharply indicated by the production of the orange-yellow coloration due to the formation of the dibromide hydrobromide.

Improved methods for the preparation of pyridine and quinoline dibromide hydrobromides are given.

The following compounds are described:  $\beta$ -*Dibromo- $\alpha$ :3:3-methylenedioxyphenylpropane*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , a colourless, viscous liquid, b. p.  $189^\circ/12$  mm., prepared from safrole and pyridine dibromide hydrobromide in the presence of glacial acetic acid at  $3-6^\circ$  and converted by successive treatment with silver acetate and potassium hydroxide into  $\beta$ -*dihydroxy- $\alpha$ :3:4-methylenedioxyphenylpropane*, m. p.  $82-83^\circ$ .  $\omega$ -*Nitro-p-methoxystyrenedibromide*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{NO}_2$ , a brown liquid which solidifies when preserved in a desiccator and is converted by an alcoholic solution of potassium acetate into  $\omega$ -*bromo- $\omega$ -nitro-p-methoxystyrene*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CBr}\cdot\text{NO}_2$ , lemon-yellow crystals, m. p.  $67.5-68^\circ$ .  $\omega$ -*Nitro-3:4-methylenedioxy-styrene dibromide*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{NO}_2$ ,

coarse, colourless prisms, which is readily converted into  $\omega$ -*bromo- $\omega$ -nitro-3:4-methylenedioxy-styrene*, yellow needles, m. p.  $101-102^\circ$ . Monobromopyrogallol, needles, decomp.  $140^\circ$  after darkening at  $120-130^\circ$ , and its *triacetate*, hexagonal plates, m. p.  $118^\circ$ . Dibromopyrogallol, m. p.  $160^\circ$  (decomp.), and its *monohydrate*, decomp.  $137^\circ$ , and *triacetate*, m. p.  $145^\circ$ . Dibromoresorcinol, long needles, m. p.  $110-112^\circ$ , and its *diacetate*, coarse prisms, m. p.  $96.5-97^\circ$ . Bromocatechol, coarse prisms, or long needles, m. p.  $87^\circ$ , and its *dibenzoate*, m. p.  $111^\circ$ . H. W.

**Orcinol.** JOHN MISSENDEN (*Chem. Age*, 1922, 7, 709; from *Chem. Zentr.*, 1923, i, 299).—Orcinol is a characteristic constituent of certain lichens of the genera *Variolaria*, *Rocella*, and *Lecanora*. It is extractable by chloroform in the form of the sodium salt, as a red solution changing to green on addition of water. It crystallises from sodium chloride solution in hexagonal tablets or prisms, m. p.  $107.3^\circ$ . The following derivatives are mentioned: *acetate*, pyramids, m. p.  $24.45^\circ$ ; *monomethyl ether*, a yellow, viscid liquid, b. p.  $285^\circ$ ; *azobenzene* derivative, red crystals, m. p.  $188.5^\circ$ ; *diethyl dicarbonate*, a viscid liquid, b. p.  $313^\circ$ . G. W. R.

**Phenols Derived from Cymene.** G. BARGELLINI (*Gazzetta*, 1923, 53, i, 234-245).—Thiele (A., 1898, i, 469) has shown that the action of acetic anhydride in presence of a small quantity of concentrated sulphuric acid converts *p*-benzoquinone into the triacetyl derivative of hydroxyquinol, the latter being then obtainable on hydrolysis. This reaction serves as a general means of introducing a new phenolic hydroxyl group into the molecule of quinols (cf. Thiele and Winter, A., 1900, i, 500, 504; Thiele and Günther, A., 1906, i, 743).

By applying this reaction to thymoquinone, the author has obtained a mixture of two triacetyl derivatives, the constitutions of which were determined by hydrolysing them and oxidising the trihydroxy-derivatives to the corresponding hydroxythymoquinones, both of which are known. The mixture of triacetyl derivatives consists of about two parts of the 2:5:6-trihydroxycymene derivative and one part of the 2:3:5-trihydroxycymene derivative; possibly the *p*-isopropyl group offers greater resistance than the methyl group to the entrance of the new substituent.

Application of Thiele's reaction to the two isomeric hydroxy-thymoquinones results, in either case, in the formation of the tetra-acetyl derivative of tetrahydroxycymene, but the latter is more easily obtained pure by passing a current of air through a cold alkaline solution of either 3- or 6-hydroxythymoquinone or of a mixture of the two.

2-Nitrosothymol, m. p. 161—162°, is readily obtained pure by gradual addition of aqueous sodium nitrite solution to a solution of thymol in a mixture of alcohol and 50% acetic acid solution. Its reduction to 2-aminothymol may be effected conveniently by means of sodium sulphide.

The *diacetyl* derivative of 2:5-thymoquinol,  $C_6H_2MePr^2(OAc)_2$ , forms white needles, m. p. 73—75°.

The *triacetyl* derivative of 2:3:5-trihydroxycymene,  $C_6HMePr^3(OAc)_3$ ,

forms white crystals, m. p. 135—137°, and is converted by hydrolysis and subsequent oxidation by ferric chloride into the 3-hydroxy-thymoquinone (O:OH:O=2:3:5) obtained by Mazzara (A., 1890, 965) from carvacrol.

The *triacetyl* derivative of 2:5:6-trihydroxycymene crystallises in white needles, m. p. 83—85°, and is convertible into 6-hydroxy-thymoquinone (O:O:OH=2:5:6).

3:6-Dihydroxythymoquinone (cf. Ladenberg and Engelbrecht, A., 1878, 60) may be conveniently prepared by passing a current of air through a solution of 3- or 6-hydroxythymoquinone in about 10% sodium or potassium hydroxide solution until the violet-red colour changes to deep garnet-red.

Reduction of the preceding compound by passage of a stream of hydrogen through its alcoholic solution containing platinum black in suspension appears to yield tetrahydroxycymene (cf. Henderson and Boyd, T., 1910, 97, 1663), but this could not be isolated, owing to the readiness with which it undergoes reoxidation to dihydroxythymoquinone. When, however, the latter is heated in a reflux apparatus with zinc dust and acetic anhydride, it yields the *tetra-acetyl* derivative of tetrahydroxycymene,  $C_{18}H_{22}O_8$ , which crystallises in white leaflets or needles, m. p. 186—188°, and dissolves in concentrated sulphuric acid to a yellow solution, this being decolorised by a drop of nitric acid. The tetra-acetyl derivative may be obtained also by dissolving either 3- or 6-hydroxy-thymoquinone in acetic anhydride and adding concentrated sulphuric acid to the hot solution. T. H. P.

**The Benzil Rearrangement. II.** ARTHUR LACHMAN (J. Amer. Chem. Soc., 1923, 45, 1509—1514).—Benzil forms, with sodium ethoxide, a white, additive product,  $OEt-CPh(ONa)-COPh$ , which is instantly decomposed, in the presence of water, into benzil, sodium hydroxide, and alcohol. When allowed to remain in dry alcoholic solution it breaks down into benzaldehyde and ethyl benzoate, only traces of benzoic acid being formed. Hence benzil sodium ethoxide does not undergo intramolecular oxidation and reduction, since migration of the sodiumoxy- or ethoxy-group would

give, respectively, sodium ethylbenzilate, or ethyl benzilate. Fission probably occurs according to the equation  $\text{OEt}\cdot\text{CPh}(\text{ONa})\cdot\text{COPh} + \text{EtOH} = \text{Ph}\cdot\text{CO}_2\text{Et} + \text{Ph}\cdot\text{CHO} + \text{EtONa}$ , although the possibility of the reaction,  $\text{OEt}\cdot\text{CPh}(\text{ONa})\cdot\text{COPh} = \text{Ph}\cdot\text{CO}_2\text{Et} + \text{Na}\cdot\text{COPh}$ , is not entirely excluded. When increasing amounts of water are added to the alcoholic solution the production of benzoic acid increases rapidly, the intermediate compound probably being  $\text{CPh}(\text{OH})_2\cdot\text{COPh}$ , or, if much sodium hydroxide is present,  $\text{OH}\cdot\text{CPh}(\text{ONa})\cdot\text{COPh}$ . These results show that the hydroxyl group, in accordance with the theory previously advanced (A., 1922, i, 459), is necessary for the intramolecular oxidation and reduction ("rearrangement") of benzil, the sodiumoxy- and ethoxy-radicals, although chemically similar, being incapable of shifting. W. S. N.

**The Benzil Rearrangement. III. ARTHUR LACHMAN (J. Amer. Chem. Soc., 1923, 45, 1522—1529).**—Hydrocyanic acid and potassium cyanide act on benzil in alcoholic solution with formation of ethyl benzoate and benzaldehyde (cf. Jourdan, A., 1883, 805; Michael and Palmer, A., 1886, 155). Benzil-cyanohydrin is probably an intermediate stage; this breaks down into benzaldehyde and benzoyl cyanide, the latter producing ethyl benzoate as a secondary reaction product. Benzoic acid is not formed in this reaction, in spite of the presence of a hydroxyl group in benzil-cyanohydrin. If, however, the latter is ionised, the ion contains no hydroxyl. The non-formation of benzoic acid may also be accounted for on the assumption that the presence of hydroxyl, although necessary, is not a sufficient condition for the intramolecular rearrangement (cf. preceding abstract).

The action of anhydrous hydrogen cyanide on benzil at  $140^\circ$  gives  $\alpha$ -cyanobenzyl benzoate,  $\text{CN}\cdot\text{CHPh}\cdot\text{O}\cdot\text{COPh}$ , m. p.  $61^\circ$ , b. p.  $300^\circ/10$  mm. or  $178^\circ/5$  mm. It is evident that benzil-dicyanohydrin is first formed; this then dissociates into benzoyl cyanide and mandelonitrile:  $\text{OH}\cdot\text{CPh}(\text{CN})\cdot\text{CPh}(\text{CN})\cdot\text{OH} = \text{Ph}\cdot\text{CO}\cdot\text{CN} + \text{Ph}\cdot\text{CHPh}\cdot\text{CN}$ , which have actually been shown to give the above ester, when heated together under similar conditions. The latter reaction excludes the possibility that the compound formed is the isomeric benzil-monocyanohydrin. W. S. N.

**The Benzil Rearrangement. IV. Benzoin. ARTHUR LACHMAN (J. Amer. Chem. Soc., 1923, 45, 1529—1535).**—It is suggested that the production of benzyl alcohol and ethyl benzoate by the action of alcoholic hydrocyanic acid on benzoin (Michael and Palmer, A., 1886, 155) proceeds similarly to the formation of benzaldehyde and ethyl benzoate from benzil (cf. preceding abstract), since benzaldehyde, which Michael and Palmer assume to be an intermediate product, does not give ethyl benzoate when heated with alcoholic hydrocyanic acid. Benzoin, like benzil, gives an additive product with sodium ethoxide.

The rearrangement of benzil is not brought about by alkali, but the action of 1.5–6.0*M*-sulphuric acid or phosphoric acid at  $175$ – $230^\circ$  leads to the formation of diphenylacetic acid, which partly decomposes into carbon dioxide and diphenylmethane.

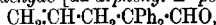
The production of the latter when benzoin is heated (Engler and Grimm, A., 1898, i, 175) undoubtedly proceeds in the same way.

The rearrangements of hydrobenzoin, with loss of water, to diphenylacetaldehyde, of benzoin to diphenylacetic acid, and of benzil, with addition of water, to benzilic acid, are held to agree with the assumption of a mobile hydroxyl group, capable of exchanging places with phenyl, whilst any theory, such as that of Tiffeneau, which has as its basis the formation of unsaturated valencies by loss of water, is inadequate.

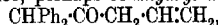
The great tendency to production of the carbonyl group is noted, numerous examples being given.

W. S. N.

**The Mechanism of the Transformation of  $\alpha$ -Glycols by the Action of Dehydrating Agents. I. The Dehydration of Allylhydrobenzoin.** S. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 369—399; cf. this vol., i, 680).—Allylhydrobenzoin,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CPh(OH)}\cdot\text{CHPh}\cdot\text{OH}$ , has been prepared by Jakubovitsch (A., 1913, i, 264) who described it as having m. p.  $88^\circ$  and giving on dehydration with dilute sulphuric acid a compound, m. p.  $126^\circ$ . It is now found that the glycol prepared by the same process has m. p.  $100^\circ$  when pure; its *monoacetate* has m. p.  $120$ — $121^\circ$ . The substance is practically not attacked by sulphuric acid under the conditions used by Jakubovitsch; more drastic treatment is necessary. The formation of the substance, m. p.  $126^\circ$ , was not observed; the reaction product consists principally of *diphenylallylacetalddehyde* [ $\alpha$ -*diphenyl- $\Delta^1$ -pentenaldehyde*],



but another substance, perhaps *benzhydryl allyl ketone*,



is also present giving a compound with semicarbazide, m. p.  $190^\circ$  (decomp.). Oxidation of the crude reaction mixture by permanganate leads to the production of benzophenone in addition to a mixture of acids; this shows that one of the reactions occurring during the dehydration of the glycol involves the wandering of a phenyl group. The lowest boiling fraction, a golden-yellow, viscous oil, b. p.  $177$ — $179^\circ/9$  mm.,  $d_4^{20}$  1.0933,  $d_4^{25}$  1.0769,  $d_4^{30}$  1.0749,  $n_D^{20}$  1.58116,  $n_D$  1.58693, consists of the practically pure aldehyde, and readily gives the *semicarbazone*, groups of needles or rhombic crystals, m. p.  $172.5^\circ$ , and the *oxime*, rosettes of colourless needles, m. p.  $126^\circ$ . The regeneration of the aldehyde from the semicarbazone was not successful. Both the oxime and the semicarbazone are readily reduced by means of hydrogen and colloidal palladium (Skita's method) to the corresponding derivatives of  $\alpha$ -diphenyl-*n*-valeraldehyde, the oxime of which melts at  $115.5^\circ$  and the semicarbazone at  $145^\circ$ . Attempts to oxidise the aldehyde to the corresponding acid failed; the oxime was therefore dehydrated by means of acetic anhydride to the *nitrile*, a colourless liquid, b. p.  $192$ — $195^\circ/14$  mm., but on treatment with hydrogen chloride in acetic acid this substance, instead of yielding the desired acid, passes into a *lactone*, opaque leaflets, m. p.  $113.5^\circ$ , probably the

lactone of  $\gamma$ -hydroxy- $\alpha\alpha$ -diphenyl-valeric acid,  $\text{CPh}_2\text{-CH-CHMe}$ ,  $\text{CO}-\text{O}$ ; it is thought that the substance, m. p. 109–110°, obtained in somewhat comparable circumstances by Ramart-Lucas (A., 1912, i, 556) may have a similar structure.

The crude aldehyde boiling at 179–181°/11 mm., is readily hydrogenated by Skita's method to the saturated  $\alpha\alpha$ -diphenylvaleraldehyde,  $\text{CPr-Ph}_2\text{-CHO}$ , b. p. 180.5°/11 mm.,  $d_4^{20}$  1.0683,  $d_4^{25}$  1.0542,  $d_4^{30}$  1.0523,  $n_D$  1.56334,  $n_D$  1.5875,  $n_F$  1.58232,  $n_g$  1.59429, forming an *oxime*, rhombic crystals, m. p. 115.5°, and a *semicarbazone*, existing in two forms, rhombic plates, m. p. 145°, and rosettes of microscopic crystals, m. p. 188°; the latter is the more sparingly soluble in alcohol.

The more soluble form is identical with the substance obtained by hydrating the semicarbazone of the unsaturated aldehyde. The substance, m. p. 188°, may perhaps be the semicarbazone of a hydrogenated substance corresponding with the unsaturated ketone probably present in the original mixture.

On oxidation with chromium trioxide in acetic acid, the saturated aldehyde passes into  $\alpha\alpha$ -diphenylvaleric acid,  $\text{CPr-Ph}_2\text{-CO}_2\text{H}$ , rhombic plates from alcohol, m. p. 155.5°; the same acid can be obtained from the oxime of the aldehyde by dehydration and hydrolysis; the *benzyl* ester has m. p. 68–69°; the *anilide*, m. p. 112°, and the *amide*, m. p. 102°, were prepared. G. A. R. K.

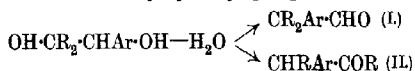
**The Mechanism of the Transformation of  $\alpha$ -Glycols by the Action of Dehydrating Agents. II. The Dehydration of isoPropylhydrobenzoin.** S. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 400–417).—isoPropylhydrobenzoin ( $\alpha\beta$ -diphenyl- $\gamma$ -methylbutane- $\alpha\beta$ -diol) is obtained in 50% yield by the action of magnesium isopropyl bromide on benzoin, and forms thin prisms, m. p. 108.5°; the *monoacetate*, prepared by means of acetyl chloride, forms small needles, m. p. 124–125°, and is accompanied by a substance, m. p. 94–95°, isomeric with the starting material. The product obtained by dehydrating the glycol with aqueous sulphuric acid consists mainly of a solid ketone, m. p. 77°, together with a liquid mixture of products.

The ketone, m. p. 77°, crystallises from alcohol in silky rods and has b. p. 170–171°/9 mm.; it is *benzhydryl isopropyl ketone* ( $\alpha\alpha$ -diphenyl- $\gamma$ -methylbutane- $\beta$ -one),  $\text{CHPh}_2\text{-CO-CHMe}_3$ . It is not readily oxidised by chromic acid; by heating with alcoholic potassium hydroxide in a sealed tube it is quantitatively split into diphenylmethane and isobutyric acid. The *oxime* forms large, prismatic plates, m. p. 128.5°; the *semicarbazone* crystallises in opaque plates, m. p. 165–166°. The ketone could not be reduced to the corresponding alcohol by means of sodium amalgam, but the use of magnesium *tert*-butyl chloride was successful.  $\alpha\alpha$ -Diphenyl- $\gamma$ -methylbutane- $\beta$ -ol boils at 180.5–181.5°/13 mm., m. p. 34°,  $d_4^{20}$  1.0591,  $d_4^{25}$  1.0446,  $d_4^{30}$  1.0427,  $n_D$  1.55986,  $n_D$  1.56502,  $n_F$  1.57741,  $n_g$  1.58818. The *benzoate*, soft needles, m. p. 105–106°, and the *phenylurethane*, fine, silky needles, m. p. 127.5°, were prepared.

The liquid mixture obtained by the dehydration of the hydrobenzoin contains considerable quantities of the ketone, m. p. 77°, which can be isolated by means of semicarbazide; another semicarbazone,  $C_{18}H_{21}ON_3$ , melting at 184—185°, can also be isolated and is probably derived from diphenylisopropylacetaldehyde ( $\alpha$ -diphenyl- $\gamma$ -methylbutaldehyde),  $CPr^2Ph_2CHO$ ; it is more abundant in the higher boiling portions of the oil. The oxidation of the oil by means of chromium trioxide gives acetone, a little benzoic acid, and benzophenone, also a neutral substance, m. p. 75—76°. The action of alcoholic potash on the oil leads to the formation of formic and isobutyric acids, benzhydrol, diphenylmethane and another hydrocarbon which was not identified. The absence of benzoic acid and diphenylisobutane amongst these products is taken as proof that no isopropyldeoxybenzoin is produced in the dehydration of isopropylhydrobenzoin; the ketone, m. p. 77°, and diphenylmethylbutaldehyde appear to constitute the bulk of the reaction mixture.

G. A. R. K.

**Semi-pinacolic Transformations. I. Dehydration of Aryldialkyl Glycols by Heat and Acids.** M. TIFFENEAU and (Mlle) J. LÉVY (*Bull. Soc. chim.*, 1923, [iv], **33**, 735—759; cf. this vol., i, 213).—Aryldialkyl glycols are intermediate in structure between hydrobenzoins and pinacones, and hence should give both semi-hydrobenzoin transformations (I) in which the tertiary hydroxyl group is eliminated as water, and semi-pinacolic transformations (II) in which the secondary hydroxyl group is so eliminated.



Reaction (I) is the more general with regard to the effect both of heat and of dilute acids. More vigorous dehydration generally leads to the formation of an ethylene oxide, but sulphuric acid in the cold causes the reaction to follow course (II). Increase of molecular weight of the group R inhibits the dehydration of the compound by heat. The following compounds are described.  $\gamma$ -Phenylhexan- $\delta$ -one, b. p. 114—116°/13 mm., oxime, m. p. 57—58°, semicarbazone, m. p. 139—140°,  $\gamma$ -phenylhexane- $\gamma\delta$ -diol, b. p. 160—161°, m. p. 49—50°;  $\alpha$ -phenyl- $\alpha$ -ethylbutaldehyde, b. p. 119—121°/14 mm., semicarbazone, m. p. 181°;  $\alpha$ -phenyl- $\beta$ -propylpentane- $\alpha\beta$ -diol, b. p. 290—300°, or 175—180°/20 mm., m. p. 100—101°;  $\delta$ -phenyloctan- $\epsilon$ -one, 154—157°/30 mm., semicarbazone, m. p. 107—108°,  $\delta$ -phenyloctane- $\delta\epsilon$ -diol, b. p. 178—179°/18 mm., m. p. 59—60°;  $\alpha$ -phenyl- $\alpha$ -propylvaleraldehydesemicarbazone, m. p. 160—161°;  $\alpha$ -phenyl- $\beta$ -n-butylhexane- $\alpha\beta$ -diol, b. p. 330—340°, or 220—230°/20 mm., m. p. 102—103°;  $\epsilon$ -phenyldecan- $\zeta$ -one, b. p. 165—170°/20 mm., semicarbazone, m. p. 100—101°, oxime, m. p. 55—56°; dibutylacetophenone, b. p. 285—290°;  $\alpha$ -anisyl- $\beta$ -ethylbutane- $\alpha\beta$ -diol, m. p. 78—79°; (?)  $\alpha$ -anisyl- $\alpha$ -ethylbutaldehyde, b. p. 165—167°/25 mm., semicarbazone, m. p. 131—133°.

H. H.

**Semi-pinacolic Transformations. II. Migrational Aptitudes of Various Acyclic Groups in Pinacolic and Semi-pinacolic Transformations.** M. TIFFENEAU and (Mlle) J. LÉVY (*Bull. Soc. chim.*, 1923, [iv], 33, 759—779; cf. preceding abstract).

—It is shown that the migrational aptitude of the ethyl and benzyl radicles is superior to that of the methyl group in both pinacolic and semi-pinacolic transformations, but that this superiority is not always exclusive. The following compounds are described.  $\alpha$ -Phenyl- $\beta$ -methyl- $\Delta^2$ -butylene, b. p. 199—200°/769 mm., 98—100°/23 mm.; nitrosite, m. p. 129—130°;  $\alpha\beta$ -oxido- $\alpha$ -phenyl- $\beta$ -methylbutane, b. p. 205—207°/760 mm.;  $\alpha$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionic acid, m. p. 95—97°; ethyl ester, b. p. 160—161°/30 mm.;  $\alpha\alpha$ -diphenyl- $\beta$ -benzylpropane- $\alpha\beta$ -diol, m. p. 81—82°;  $\alpha\beta\beta$ -triphenylbutan- $\gamma$ -one, m. p. 64°;  $\alpha\gamma$ -diphenyl- $\beta$ -methylpropan- $\beta$ -ol, b. p. 194—199°/20 mm.;  $\alpha\gamma$ -diphenyl- $\beta$ -methylpropylene,



b. p. 180—183°/25 mm., nitrosite, m. p. 122—123°. H. H.

**Reduction Products of Benzylidenepinacolin.** G. A. HILL, C. S. SPEAR, and J. S. LACHOWITZ (*J. Amer. Chem. Soc.*, 1923, 45, 1557—1562).—The reduction of benzylidenepinacolin by means of hydrogen and palladium black in alcoholic solution leads to the formation of  $\omega$ -benzylpinacolin, a fragrant, nearly colourless, highly refractive liquid, b. p. 153°/40—42 mm., or 247° at atmospheric pressure, *oxime*, slender, white crystals, m. p. 95°. The constitution of this ketone is proved by its synthesis, by the action of benzyl chloride in ethereal solution on the sodium derivative of pinacolin, prepared in ethereal solution by the action of sodamide. Reduction of benzylidenepinacolin by means of aluminium amalgam, magnesium amalgam, sodium amalgam, sodium and ethyl alcohol, sodium and moist ether, or zinc and acetic acid gives the same product, together with a white, finely crystalline substance, m. p. 142°, presumably  $\beta$ -phenylethyl-*tert*-butylcarbinol, and the dimeric product,  $\beta\beta$ -tetramethyl- $\epsilon$ -[diphenyldecan- $\gamma$ -dione, a white, microcrystalline compound, which is also formed by the action of sodium on  $\alpha$ -chloro- $\alpha$ -phenyl- $\delta\delta$ -dimethylpentan- $\gamma$ -one in ethereal solution.

W. S. N.

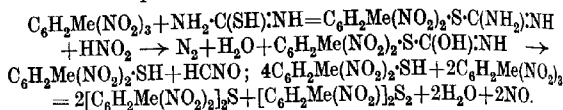
**The Action of Potassium Hydroxide on Tetratolyl- and Tetraphenylbutenediols.** G. ARBUZOV and (Mlle) T. TEMERKOVA (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 219—222).—It is found that tetra-*p*-tolylbutenediol, prepared by the action of magnesium acetylene dibromide (locitsch, A., 1914, i, 393) on di-*p*-tolyl ketone, small needles, m. p. 156°, is not decomposed by aqueous potassium hydroxide; the solid alkali causes decomposition at 125° into di-*p*-tolyl ketone and acetylene. The glycol in ethereal solution readily forms a monopotassium salt from which it is regenerated by water, whilst on heating, the dry salt decomposes into acetylene and di-*p*-tolyl ketone. The glycol appears to possess only one active hydroxyl group as shown by the Zerevitinov-Tschugaev test.

The tetraphenyl compound also forms a monopotassium salt

and is decomposed by solid potassium hydroxide at a somewhat higher temperature than the preceding compound, the product being acetylene and benzophenone.

G. A. R. K.

**New Method of Preparation of certain Aromatic Sulphides.**  
I and II. MICHELE GIUA and ANTONIO RUGGERI (*Gazzetta*, 1923, **53**, i, 290—296; 341—345).—I. When heated together in presence of a little alcohol, thiocarbamide and 3:4:6-trinitrotoluene interact, giving, in addition to various secondary products, a mixture of di-4:6-dinitro-*m*-tolyl sulphide and di-4:6-dinitro-*m*-tolyl disulphide, the reaction apparently taking place in accordance with the equations:



The *N*-substituted derivatives of thiocarbamide also react with 3:4:6-trinitrotoluene, the principal product obtained in the case of allylthiocarbamide being di-4:6-dinitro-*m*-tolyl sulphide.

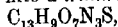
The interaction of 3:4:6-trinitrotoluene and thiophenol in alcoholic solution is expressed by the equation,  $2\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3 + 4\text{Ph}\cdot\text{SH} = 2\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2\cdot\text{SPh} + \text{Ph}\cdot\text{S}\cdot\text{S}\cdot\text{Ph} + 2\text{H}_2\text{O} + 2\text{NO}$ , the yield of the sulphide being almost theoretical. Ethyl mercaptan does not react when heated with 3:4:6-trinitrotoluene.

*Di-4:6-dinitro-m-tolyl sulphide* crystallises in pale yellow prisms, *m. p.* 189—190°, and in alcoholic solution gives a reddish-brown coloration with alkali.

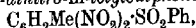
The *disulphide* crystallises in lustrous, yellow lamellæ, *m. p.* 263—265° (rapid heating), and is readily attacked by fuming nitric acid, with formation of 4:6-dinitro-*m*-tolylsulphonic acid, *m. p.* 120—135°.

*Di-4:6-dinitro-m-tolyl sulfoxide*  $[\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2]_2\text{SO}$ , obtained by the action of nitric acid (*d* 1.5) on the sulphide, forms lustrous, white prisms, *m. p.* above 260° (decomp.).

*Phenyl 4:6-dinitro-m-tolyl sulphide*,  $\text{SPh}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$ , prepared from 3:4:6-trinitrophenol and thiophenol, crystallises in lustrous, yellow laminae, *m. p.* 142—143°, and in alcoholic solution gives a dark red coloration with alkali. By excess of nitric acid (*d* 1.5) in the cold it is converted into a *trinitrophenyl m-tolylsulphoxide*,



crystallising in lustrous needles, *m. p.* 203—204°; the new nitro-group probably occupies the para-position in the second phenyl residue. *Phenyl 4:6-dinitro-m-tolylsulphone*,



prepared by the action of chromic anhydride on the sulphide in acetic acid solution, crystallises in small lamellæ, *m. p.* 164—165°.

II. When 1-chloro-2:4-dinitrobenzene (1 mol.) is heated on the water-bath with thiocarbamide (1 mol.), 2:4-dinitrophenyl mercaptan, 2:4:2':4'-tetranitrodiphenyl disulphide and a small proportion of 2:4:2':4'-tetranitrodiphenyl sulphide are formed.

The last of these compounds, however, constitutes the principal product when the proportion of the thiocarbamide is halved and the reaction is carried out in presence of ethyl alcohol and sodium acetate; the formation of the sulphide is due to the action of the chlorodinitro-compound on the mercaptan formed in the first stage of the reaction. In the former case, the reactions are expressed by the equations:  $C_6H_3Cl(NO_2)_2 + SH \cdot C(NH_2)_2NH \rightarrow C_6H_3(NO_2)_2 \cdot S \cdot C(NH_2)_2NH \rightarrow C_6H_3(NO_2)_2 \cdot SH + NC \cdot NH_2$  and  $NC \cdot NH_2 + HCl + Et \cdot OH = OEt \cdot C(NH_2)_2NH \cdot HCl$  (cf. Stieglitz and McKee, A., 1900, i, 340, 431; Stieglitz and Noble, A., 1905, i, 639; McKee, A., 1901, i, 755; 1909, i, 635; Brucc, A., 1904, i, 491, 573). At the temperature of boiling alcohol, the reaction proceeds according to the equation  $C_6H_3(NO_2)_2Cl + CS(NH_2)_2 + Et \cdot OH = C_6H_3(NO_2)_2 \cdot SH + OEt \cdot C(NH_2)_2NH \cdot HCl$ , which is analogous to that given by Willgerodt (A., 1878, 141) for the temperature range 150–200°. T. H. P.

**Deaminisation of Methyl *d*-cis-3-Amino-1 : 2 : 2-trimethylcyclopentane-1-carboxylate.** GLENN S. SKINNER (*J. Amer. Chem. Soc.*, 1923, 45, 1498–1509).— $\alpha$ -*d*-Camphoramidic acid is converted by treatment with sodium hypobromite into *d*-cis-3-amino-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid, the hydrochloride of which gives, by esterification by means of methyl alcohol and hydrogen chloride, the hydrochloride of methyl *d*-cis-3-amino-1 : 2 : 2-trimethylcyclopentane-1-carboxylate, m. p. 237–238°,  $[\alpha]_D^{25} + 29.4^\circ$  (0.05 g./c.c. absolute alcohol),  $[\alpha]_D^{25} + 29.2^\circ$  (0.10 g./c.c. absolute alcohol),  $[\alpha]_D^{25} + 20.4^\circ$  (0.04 g./c.c. water). When this hydrochloride is treated with aqueous sodium nitrite on a large scale, no ether of a free hydroxy-acid is produced. The products are formed in the following proportions: esters of unsaturated acids, 62%; esters of hydroxy-acids, 36%; esters of chloro-acids, 2% (cf. Noyes and Skinner, A., 1918, i, 65).

The unsaturated ester obtained has b. p. 85°/21 mm., 75°/15 mm., 72°/12 mm., 65°/9 mm., 56°/5.5 mm., or 51°/4 mm.,  $d_4^{20}$  0.9607,  $n_D^{25}$  1.4484,  $n_D^{55}$  1.45267,  $n_{501}$  1.4580,  $n_{488}$  1.4590,  $n_{477}$  1.4631 at 25°. The mixture of unsaturated acids, obtained by hydrolysis by means of ethyl-alcoholic sodium hydroxide, has b. p. 108°/4 mm.,  $[\alpha]_D^{25} + 97.3^\circ$ ,  $[\alpha]_D^{25} + 93.6^\circ$ ,  $[\alpha]_D^{25} + 74.9^\circ$ ,  $[\alpha]_D^{25} + 71.6^\circ$  (0.0976 g./c.c. absolute alcohol), and consists of *d*-lauronic acid and 1 : 2 : 3-trimethyl- $\Delta^4$ -cyclopentane-1-carboxylic acid, in the ratio 7 : 3. The presence of the latter is proved by the production of  $\alpha$ -carboxy- $\alpha\beta\beta$ -trimethylglutaric acid, on oxidation by means of alkaline potassium permanganate. Moreover, the action of bromine in ice-cold chloroform solution gives a dibromo-acid, large, transparent crystals, m. p. 189°,  $[\alpha]_D^{25} + 94.1^\circ$ ,  $[\alpha]_D^{25} + 91.6^\circ$  (0.0994 g./c.c. absolute alcohol), which is converted by means of sodium carbonate into the lactone of 5-bromo-4-hydroxy-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid. A second product of the bromination is the lactone of 2-bromo-3-hydroxy-1 : 2 : 3-trimethylcyclopentane-

1-carboxylic acid (*loc. cit.*), which is derived from lauronic acid, and passes on boiling with water into the *lactone* of 2 : 3-dihydroxy-1 : 2 : 3-trimethylcyclopentane-1-carboxylic acid, long needles, m. p. 214—215°. The action of sodium ethoxide on the other bromolactone gives the sodium salt of the dihydroxy-acid, from which the *lactone* of 4 : 5-dihydroxy-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid, long, six-sided, monoclinic prisms, m. p. 225—226°, is obtained on acidification.

The ester fraction which boils at 88—89°/2·5—3 mm. gives, on hydrolysis, *d-cis*-2-hydroxy-1 : 2 : 3-trimethylcyclopentane-1-carboxylic acid (*loc. cit.*), which has  $[\alpha]_D^{25} + 35\cdot7$  (0·0569 g./c.c. absolute alcohol). This fraction of ester contains the largest percentage (6%) of esters of chloro-acids,  $C_8H_{14}Cl\cdot CO_2Me$ . The *methyl* ester boiling at 108—110°/4 mm. has  $d_4^{20} 1\cdot0711$ ,  $[\alpha]_D^{25} + 29\cdot9^\circ$ ,  $[\alpha]_D^{25} + 29\cdot6^\circ$  (0·967 g./c.c. absolute alcohol), and gives, on hydrolysis, *i*-2-hydroxy-1 : 5 : 5-trimethylcyclopentane-1-carboxylic acid, m. p. 209—210°, which does not pass into a lactone when heated at 255°, but sublimes unchanged. On oxidation by means of Beckmann's chromic acid mixture, it gives an *acid*, m. p. 218°, which is not oxidised to camphoronic acid by means of potassium permanganate. The *methyl* ester boiling at 105—107°/5 mm. has  $[\alpha]_D^{25} + 22\cdot4^\circ$ , and gives, on hydrolysis, *l-trans*-3-hydroxy-1 : 5 : 5-trimethylcyclopentane-1-carboxylic acid, silky tufts of slender needles, m. p. 121—122°, b. p. 165°/5 mm.,  $[\alpha]_D^{25} - 10\cdot3^\circ$  (0·0329 g./c.c. absolute alcohol), which is not converted into a lactone when heated at 225°. Oxidation of this acid by means of Beckmann's chromic acid mixture gives a gummy acid, which is further oxidised by means of potassium permanganate to camphoronic acid. The hydroxy-acid is converted by means of hydrogen iodide in carbon disulphide solution into the unstable *iodide*, which, on treatment with alkalis, gives an unsaturated acid, probably the  $\Delta^2$ -acid,  $[\alpha]_D 35^\circ$  (0·0091 g./c.c. absolute alcohol), and a small quantity of an inactive *lactone*, m. p. 47—48°.

An *acid*, m. p. 132—133°, has also been isolated, but in such small amount that characterisation was impossible. W. S. N.

**Preparation of *n*-Butyl *p*-Aminobenzoate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Swiss Pat. 96144; from *Chem. Zentr.*, 1923, ii, 480; cf. A., 1922, i, 827—828).—*n*-Butyl *p*-nitrobenzoate is prepared by heating *p*-nitrobenzoic acid or *p*-nitrobenzoyl chloride with *n*-butyl alcohol in the presence of strong sulphuric acid. It forms colourless leaflets, m. p. 35°; b. p. 160°/8 mm. Reduction by the usual methods gives the amino-ester.

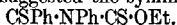
G. W. R.

**Preparation of Ethyl *p*- $\beta$ -Diethylaminoethylaminobenzoate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Swiss Pat. 93120; from *Chem. Zentr.*, 1923, ii, 479—480).—Ethyl *p*- $\beta$ -chloroethylaminobenzoate,  $CH_2Cl\cdot CH_2\cdot NH\cdot C_2H_4\cdot CO_2Et$ , is treated with diethylamine under pressure at 100°. Ethyl *p*- $\beta$ -diethylaminoethylaminobenzoate is an oily liquid. The *hydrochloride* forms white needles, m. p. 156°.

G. W. R.

**The Constitution of some Iminosulphides.** H. RIVIER and J. SCHALCH (*Helv. Chim. Acta*, 1923, 6, 605—617).—The two isomeric methylthiobenzanilides are readily decomposed by heat without isomerisation in either case. The two benzylthiobenzanilides have now been prepared, and are also found not to be interconvertible by heat. *S-Benzylthiobenzanilide*,  $\text{CPh}\cdot\text{NPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ , was prepared by the action of benzyl chloride on an alcoholic sodium hydroxide solution of thiobenzanilide. It crystallises in pale yellow needles, m. p.  $53^\circ$ , and forms a yellow, crystalline *hydrochloride*, m. p.  $131\text{--}132^\circ$  (decomp.). *N-Benzylthiobenzanilide* was prepared by the action of phosphorus pentasulphide on benzylbenzanilide in boiling carbon disulphide. It forms yellow crystals, m. p.  $121\text{--}122^\circ$ , and does not form a hydrochloride.

The constitution,  $\text{NPh}\cdot\text{CPh}\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$ , for the "iminoxanthide" obtained by Tschugaev (A., 1902, i, 604) by the action of aromatic iminochlorides on an alkali xanthate has been criticised by Jamieson (A., 1904, i, 396), who suggested the symmetrical formula

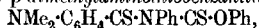


The latter formula has now been confirmed by preparing such compounds in three different ways. The same compound is given by (1) Tschugaev's method; (2) the action of an ester of chlorothiocarbonic acid,  $\text{OR}\cdot\text{CSCl}$ , on the sodium salt of a thioanilide, and (3) by the action of an ester of phenyliminochlorocarbonic acid,  $\text{NPh}\cdot\text{CCl}\cdot\text{OR}$ , on lead dithiobenzoate. If Tschugaev's formula were correct, the first and third methods should give two isomeric substances,  $\text{NPh}\cdot\text{CPh}\cdot\text{S}\cdot\text{CS}\cdot\text{OR}$  and  $\text{CSPh}\cdot\text{S}\cdot\text{C}(\text{NPh})\cdot\text{OR}$ . It is to be supposed that these both undergo transformation into



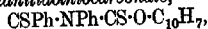
and the product should be called a dithiodiacylanilide. The two new methods for their preparation allow substances in which R is an aromatic radicle to be obtained. Tschugaev's compound, which is now called *ethyl thiobenzanilidothiocarbonate*, is found to be dimorphous, one form being garnet and the other bright red. By the first method were prepared *ethyl  $\alpha$ -thiobenzonaphthalidothiocarbonate*,  $\text{CSPh}\cdot\text{N}(\text{C}_{10}\text{H}_7)\cdot\text{CS}\cdot\text{OEt}$ , red prisms, m. p.  $142^\circ$ , from  $\alpha$ -benzonaphthalide, and *ethyl  $\beta$ -thiobenzonaphthalidothiocarbonate*, red crystals, m. p.  $123\text{--}124^\circ$ , from  $\beta$ -benzonaphthalide and potassium ethylxanthate.

*Phenyl thiobenzanilidothiocarbonate*, from phenyl chlorothiocarbonate and thiobenzanilide, forms bright red needles, m. p.  $112\text{--}113^\circ$ ; *phenyl p-dimethylaminothiobenzanilidothiocarbonate*,



forms red crystals, m. p.  $121\text{--}122^\circ$ ; it dyes silk. *Phenyl  $\beta$ -thiobenzonaphthalidothiocarbonate*,  $\text{CSPh}\cdot\text{N}(\text{C}_{10}\text{H}_7)\cdot\text{CS}\cdot\text{OPh}$ , crystallises in bright red needles, m. p.  $145\text{--}146^\circ$ .

*$\beta$ -Naphthyl chlorothiocarbonate*,  $\text{CSCl}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$ , was prepared by the action of thiocarbonyl chloride on sodium  $\beta$ -naphthoxide solution; it forms yellow crystals, m. p.  $76\text{--}77^\circ$ . *Ethyl naphthyl thiocarbonate*,  $\text{OEt}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$ , forms colourless needles, m. p.  $67^\circ$ .  *$\alpha$ -Naphthyl chlorothiocarbonate* is difficult to prepare; it boils at  $165\text{--}166^\circ/13$  mm. and forms a mass of yellow crystals.

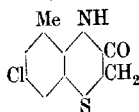
*β-Naphthyl thiobenzamidothiocarbonate,*

forms reddish-brown crystals, m. p. 131—132°; *β-naphthyl β-thio-benzonaphthalidothiocarbonate* forms reddish-brown crystals, m. p. 163—164°; *β-naphthyl α-thiobenzonaphthalidothiocarbonate*, bright red crystals, and *α-naphthyl β-thiobenzonaphthalidothiocarbonate*, bright red crystals, m. p. 134—135°. E. H. R.

**Polymerisation of Allyl Cinnamylideneacetate.** F. F. BLICKE (*J. Amer. Chem. Soc.*, 1923, 45, 1562—1566).—*Allyl cinnamylideneacetate*, b. p. 210°/20 mm., is a light yellow liquid having a high index of refraction. It reacts with bromine in light petroleum solution to give the *hexabromide*, crystals possessing a silky lustre, m. p. 126°. When heated, the ester polymerises to an amorphous, amber-like material having the same composition as the original ester. The polymerised ester is readily hydrolysed to an amorphous acid, having the same composition as cinnamylideneacetic acid. When the amorphous acid is heated with barium hydroxide a mixture of liquid compounds, evidently hydrocarbons, is produced with elimination of carbon dioxide. The analysis of the mixture gives figures not very far removed from those required for phenylbutadiene. W. S. N.

**Preparation of Arylthioglycollic [Arylthiolacetic] Acids.**

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360425; from *Chem. Zentr.*, 1923, ii, 407).—Diazo-compounds of *o*-amino-arylthiolacetic acids are treated with ethyl alcohol and copper. Arylthiolacetic acids,  $\text{R-S-CH}_2\text{-CO}_2\text{Et}$ , are thereby obtained without accompanying formation of hydroxy- or alkoxy-compounds. The reaction takes place usually in the presence of sulphuric acid. *Phenylthiolacetic acid* is obtained from 2-aminophenylthiolacetic acid; 4-chlorophenylthiolacetic acid from 4-chloro-2-amino-1-phenylthiolacetic acid; *s*-5-chloro-*m*-tolylthiolacetic acid by the action of sulphur monochloride on *o*-toluidine, reduction of the products of reaction with zinc dust or sodium hyposulphite, and treatment with monochloroacetic acid. Treatment of the sodium salt of 5-chloro-2-amino-*m*-tolylthiolacetic acid with acids gives 7-chloro-3-keto-5-methylidihydro-1:4-iso-benzthiazine (annexed formula); it forms small needles, m. p. 238°. G. W. R.

**Preparation of Halogen Alkyl Esters of Aromatic *o*-Hydroxycarboxylic Acids.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 360491; from *Chem. Zentr.*, 1923, ii, 479).—

*o*-Hydroxybenzoic acid or its acyl compounds, or its homologues and derivatives, are esterified by known methods with iodohydrins or esters, chlorinated or brominated in the alcohol group, are treated with iodides. *Iodoethyl salicylate*, a colourless liquid, b. p. 180—183°/20 mm., is obtained by heating chloroethyl salicylate with sodium iodide in alcoholic solution or by esterification of ethylene iodohydrin either with salicyloyl chloride in the presence of benzene

or pyridine, or with salicylic acid in the presence of hydrogen chloride, or by heating sodium salicylate with ethylene chloroiodide. By acetylation, it gives *iodoethyl o-acetoxybenzoate* (crystals, m. p. 37—38°) which may also be obtained from *chloroethyl o-acetoxybenzoate* (crystals, m. p. 62°).  $\alpha$ -Iododihydroxypropane gives with *o*-acetoxybenzoyl chloride the ester of propenyl- $\alpha$ -iodohydrin, a thick, yellow oil. *Di-iodopropyl o-acetoxybenzoate* is a viscous, yellow oil. *Chloroethyl 4-hydroxy-m-toluate*, an oil with b. p. 136—139°/10 mm., from 4-hydroxy-*m*-toluic acid and ethylene chlorohydrin, gives, with sodium iodide and amyl alcohol, *iodoethyl 4-hydroxy-m-toluate*, b. p. 166—169°/10 mm. The latter, by acetylation, gives *iodoethyl 4-acetoxy-m-toluate*, a yellow oil decomposing on distillation.

G. W. R.

**Di-iodohydrin Salicylate.** WINCENTY HUMNICKI (*Istý Zjazd Chemikóv Polskich*, 1923, 62).—*Di-iodohydrin salicylate* is prepared by the iodination of glycerol in the presence of salicylic acid. The same ester can probably be prepared by the direct esterification of salicylic acid with di-iodohydrin.

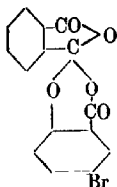
R. T.

**Substituted Salicylic Acids. II.** H. P. KAUFMANN (*Ber. Deut. pharm. Ges.*, 1923, 33, 120—132).—To decide between the two formulæ possible for the compound obtained by the action of *o*-phthalyl chloride on sodium or disodium salicylate (A., 1922, i, 252), use is made of the reaction discovered by Pfeiffer (A., 1914, i, 551; 1917, i, 205), who found that both maleic and phthalic anhydrides, which contain the quinonoid linking,  $O:\dot{C}:\dot{C}:\dot{C}:\dot{C}:O$ , give with aromatic hydrocarbons, phenols and amides, more or less deep colorations obeying the regularities determined for the quinhydrones. Further, phthalaldehyde, which contains the above grouping, dissolves in dimethylaniline giving an orange-yellow coloration, whereas phthalide, which lacks such grouping, remains colourless with this reagent (A., 1919, i, 62). Since it is found that the above compound, m. p. 158.5°, gives no coloration with the solvents used by Pfeiffer, the phthalyl chloride used in its formation must react in its asymmetric form, the compound itself having the structure II (A., 1922, i, 253); it is proposed to call it salicylic acid phthalidylidene-ether-ester.

The latter exhibits extremely high stability and resists hydrolysis, being decomposed only by energetic reducing agents. Its 5-bromo- and 3:5-dibromo-derivatives may be prepared by using the corresponding derivatives of salicylic acid instead of the latter itself. The 5-nitro-derivative gives on reduction the 5-amino-derivative, which shows the usual reactions for primary amines, but is only sparingly soluble in hydrochloric acid. Diazotisation of the amino-compound and coupling of the diazo-salt with aniline and with  $\beta$ -naphthol yields red or cocoa-brown colouring matters.

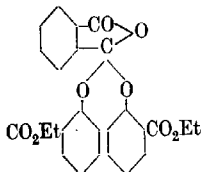
The reaction between *o*-phthalyl chloride and salicylic acid is not altered by substitution in the former, but proceeds quite differently when esters of salicylic acid are used. In this case, two mols. of the ester react with the phthalyl chloride in the asymmetric

configuration, giving esters of phthalaldisalicylic acid. In preparing these derivatives, it is found that esters of the salicylic acids react with difficulty with phthalyl chloride, whereas the sodium salts of the esters react more rapidly. With terephthalyl or isophthalyl chloride, two molecules of the salicylic acids or their esters always react.

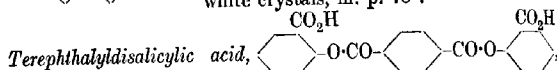


*5-Bromosalicylic acid phthalidylidene-ether-ester* (annexed formula) forms crystals, m. p. 176°, and the corresponding 3:5-dibromo-compound, crystals, m. p. 217°.

*5-Nitrosalicylic acid phthalidylidene-ether-ester*,  $C_{15}H_9O_5N$ , is obtained as a white, sandy compound, m. p. 214.5°; the 5-amino-compound,  $C_{15}H_{11}O_5N$ , melts gradually with decomposition, and on diazotisation yields with aniline the reddish-brown compound,  $C_{15}H_9O_5N:N-NHPh$ , and with  $\beta$ -naphthol the cocoa-brown compound,  $C_{15}H_9O_5N:N-C_{10}H_6-OH$ , neither of which has a definite melting point.



*Ethyl o-phthalaldisalicylate* (annexed formula) forms crystals, m. p. 56°; the *phenyl* ester,  $C_{34}H_{22}O_8$ , crystals, m. p. 112°, and the  $\beta$ -*naphthyl* ester,  $C_{42}H_{26}O_8$ , white crystals, m. p. 78°.

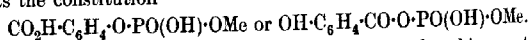


*Terephthalaldisalicylic acid*,  $C_{26}H_{16}O_8$ , is a white, amorphous compound, decomposing at 180—190°; its *ethyl* ester,  $C_{26}H_{20}O_8$ , crystallises in nodular masses, m. p. 165°, and its *phenyl* ester,  $C_{34}H_{22}O_8$ , in white needles, m. p. 189—190°; its  $\beta$ -*naphthyl* ester,  $C_{42}H_{26}O_8$ , forms crystals, m. p. 80°.

*Ethyl isophthalaldisalicylate*,  $C_{26}H_{22}O_8$ , forms colourless needles, m. p. 90°; the *phenyl* ester, a pale yellow oil, and the  $\beta$ -*naphthyl* ester,  $C_{42}H_{26}O_8$ , crystals, m. p. 130°.

T. H. P.

**Monomethylorthophosphosalicylic Ester.** ÉMILE GAUTRELET (*Compt. rend.*, 1923, 176, 1770—1772).—The interaction of 3 mols. of monomethyl orthophosphate with 3 mols. of sodium salicylate results in the formation of 1 mol. of trisodium phosphate, 1 mol. of methyl salicylate and 2 mols. of methylorthophosphosalicylate, which, according as the temperature is higher or lower, has the constitution



The former substance forms short, colourless, rhombic crystals, m. p. 113°, and gives in solution scarcely any coloration with ferric chloride. The latter substance forms long needles, m. p. 98°, and gives a violet coloration with ferric chloride. The therapeutic value of the two isomerides is identical, however, their action being both antipyretic and analgesic.

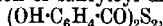
G. F. M.

**Iodosalicylic Acids.** P. BRENANS and C. PROST (*Compt. rend.*, 1923, 176, 1626—1629; cf. Goldberg, A., 1879, 928; Miller, T., 1882, 41, 398).—5-Iodosalicylic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CO}_2\text{H}$ , was prepared, by treating the hydrochloride of 5-aminosalicylic acid with sulphuric acid, diazotising, and adding hydriodic acid. It forms white needles, m. p.  $198^\circ$ ; the acetyl derivative crystallises in needles, m. p.  $166^\circ$ ; the ethyl ester (cf. Schmitt, *Z. für Chemie*, 1864, 322), prepared by boiling the acid with absolute alcohol containing 15% of sulphuric acid, forms long, colourless needles of aromatic odour, m. p.  $70-71^\circ$ . The isomeride 3-iodosalicylic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CO}_2\text{H}$ , prepared similarly from the sulphate of the corresponding amino-acid, crystallises in needles, m. p.  $199^\circ$ , yields an acetyl derivative, white plates, m. p.  $135^\circ$ , and an ethyl ester which was obtained as a colourless oil. The two acids on addition of iodine yield the same 3:5-di-iodosalicylic acid,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{CO}_2\text{H}$ , white needles, m. p.  $228^\circ$ , acetyl derivative, hard, white plates, m. p.  $153^\circ$ .  
H. J. E.

**Acetylation with Acetic Anhydride and Sulphuric Acid.** O. FERNÁNDEZ and C. TORRES (*Anal. Fis. Quím.*, 1923, 21, 22—32).—The authors have used acetic anhydride in the presence of small quantities of sulphuric acid for the preparation of a number of acetyl compounds. For example, in the preparation of *o*-acetoxybenzoic acid, 30 g. of salicylic acid are treated with 44.4 g. of acetic anhydride, 15 drops of strong sulphuric acid being then added to the mixture. The authors describe the acetylation of resorcinol, pyrogallol, *o*- and *p*-nitrophenols, morphine, and quinine.

G. W. R.

**Preparation of Thiolsalicylic Acid.** CHEMISCHE FABRIK VON FRIEDRICH HEYDEN (D.R.-P. 365212; from *Chem. Zentr.*, 1923, ii, 251—252).—An alcoholic solution of an alkali hydro-sulphide is allowed to act on salicyloyl chloride or an acyl-salicyloyl chloride. Thiolsalicylic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{SH}$ , forms white crystals, m. p.  $33^\circ$ , with an odour like phosphorus. With ferric chloride, a reddish-violet coloration is obtained which disappears with precipitation of salicyloyl disulphide,



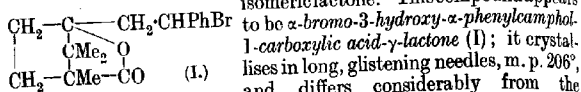
m. p.  $129^\circ$ . The alkali and alkaline-earth salts readily decompose, giving sulphur and hydrogen sulphide.

G. W. R.

**Brominated Lactones from Benzylidenecampholic Acid.** H. RUPE and A. SULGER (*Helv. Chim. Acta*, 1923, 6, 435—442).—It was hoped, by elimination of 2 mols. of hydrogen bromide from  $\alpha$ , $\beta$ -dibromobenzylcampholic acid (Rupe and Blechschmidt, A., 1918, i, 223), to obtain a compound containing the acetylenic linking, but instead, by the action of alcoholic potassium hydroxide, only 1 mol. of hydrogen bromide was eliminated, with formation of  $\alpha$ -bromo- $\alpha$ -phenyl- $\beta$ -hydroxycamphol-1-carboxylic acid- $\delta$ -lactone,  $\text{CO}\langle\text{C}_6\text{H}_4\text{O}\rangle\text{CH}\cdot\text{CHPhBr}$ , which has m. p.  $141^\circ$ , not  $139^\circ$ , as previously given. The lactone forms the magnesium

salt of  $\alpha$ -bromo- $\beta$ -hydroxy- $\alpha$ -phenylhomocampholic acid when treated carefully with magnesium oxide and water. When reduced with sodium amalgam, the lactone is converted into benzylidene-campholic acid. This unusual reaction is probably due to the intermediate formation of  $\beta$ -hydroxy- $\alpha$ -phenylhomocampholic acid, which readily loses water, forming benzylidenecampholic acid. When the lactone is boiled with an excess of magnesium oxide for a long time, the  $\delta$ -lactone of  $\alpha$ - $\beta$ -dihydroxy- $\alpha$ -phenylcamphol-1-carboxylic acid is formed, white needles, m. p. 156°.

When benzylidenecampholic acid is exposed for a long time to bromine vapour, at first the dibromo-additive compound is formed, but later hydrogen bromide is eliminated with formation of an isomeric lactone. This compound appears



to be  $\alpha$ -bromo-3-hydroxy- $\alpha$ -phenylcamphol-1-carboxylic acid- $\gamma$ -lactone (I); it crystallises in long, glistening needles, m. p. 206°, and differs considerably from the  $\delta$ -lactone in solubility. When boiled with magnesium oxide and water it gives a crystalline compound, m. p. 135°, free from bromine, which has not yet been further examined. When reduced with sodium amalgam it gives benzylidenecampholic acid. By boiling alcoholic potassium hydroxide it is converted into a crystalline product, m. p. 188°, which is assumed to be  $\alpha$ -phenyl- $\alpha$ -3-dihydroxycamphol-1-carboxylic acid. Alkalis do not remove bromine from the  $\delta$ -lactone in this way. E. H. R.

**Hydroxynaphthoic Acids. II.** CARLTON BUTLER and FRANK ALBERT ROYLE (T., 1923, 123, 1649—1657).

**The Formation of Derivatives of Tetrahydronaphthalene from  $\gamma$ -Phenyl Fatty Acids. III. The Influence of Substituents on Ring Closure.** ARTHUR JOHN ATTWOOD, ARNOLD STEVENSON, and JOCELYN FIELD THORPE (T., 1923, 123, 1755—1766).

**Ring-chain Tautomerism. VI. The Mechanism of the Keto-cyclol Change in the Propane Series.** ERIC WILLIAM LANFEAR and JOCELYN FIELD THORPE (T., 1923, 123, 1683—1689).

**A Simple Preparation of Pyromellitic Acid.** HENRI DE DIESBACH, VICTOR SCHMIDT, and EUGÈNE DECKER (*Helv. Chim. Acta*, 1923, 6, 548—549).—When technical xylene is brominated in the cold, a solid fraction is obtained consisting of a mixture of 4:6-dibromo-*m*-xylene, 2:5-dibromo-*p*-xylene, and 4:5-dibromo-*o*-xylene. By heating this mixture with cuprous cyanide and pyridine at 200°, a mixture of the nitriles of  $\alpha$ - and  $\beta$ -cumidic acids is obtained, m. p. 148—150°. The dibromo-*o*-xylene gives dimethylphthalimide, which remains in the mother-liquor. Hydrolysis of the mixed nitriles with boiling 70% sulphuric acid gives a mixture of  $\alpha$ - and  $\beta$ -cumidic acids which are oxidised by potassium permanganate to pyromellitic acid. E. H. R.

**The Molecular Weight of Benzaldehyde-Copper and the Formation of Benzaldehyde-Copper-Pyridine.** FRITZ SCHAAF (*Helv. Chim. Acta*, 1923, 6, 535–538).—The molecular weight of benzaldehyde-copper (A., 1922, i, 1029) was determined cryoscopically in camphor, and was found to correspond with the formula  $C_7H_5O_2Cu$ . The solubility of the compound in the usual solvents is too low for molecular-weight determinations by the ebullioscopic method. The density of the compound is  $d_4^{20} 1.4552$ . In hot pyridine, it dissolves with a blue colour, and from the solution, on cooling, there separate deep blue silky needles of *benzaldehyde-copper-pyridine*,  $2C_{14}H_{12}O_2Cu \cdot 5C_5H_5N$ . This is stable in air, is decomposed by acids and alkalis, but is soluble in ammonium hydroxide. When heated at  $150^\circ$ , it loses pyridine, leaving a residue of pure benzaldehyde-copper. Similar compounds appear to be formed with other organic bases, such as aniline, quinoline, and collidine, in which benzaldehyde-copper dissolves, forming green or blue solutions. E. H. R.

**The Catalytic Reduction of Acid Chlorides. VI. The Preparation of Unsaturated Aldehydes.** KARL W. ROSENMUND, FRITZ ZETZSCHE, and G. WEILER (*Ber.*, 1923, 56, [B], 1481–1487; cf. A., 1922, i, 431 and previous abstracts).—The authors' method of preparing aldehydes from acid chlorides has been extended to unsaturated aldehydes. Satisfactory and uniform results are only obtained when pure palladium preparations are used in conjunction with suitable addenda. Less pure catalysts, including such as are quite suitable for other reductions, appear to cause the production of greater proportions of complex products and less aldehyde. Care is also necessary with regard to the addenda, since freshly prepared "sulphured quinoline" is more uniform in its action than older specimens. On the other hand, crystalline thiouanthrene gives uniformly good results.

*Acetylvanillyl chloride*, colourless crystals, m. p.  $57^\circ$  (corresponding amide, m. p.  $175^\circ$ ; *anilide*, m. p.  $160$ – $161^\circ$ ), is reduced by hydrogen in the presence of xylene, palladised barium sulphate, and sulphured quinoline to vanillin, m. p.  $80^\circ$ , the yield being 82.5% of that theoretically possible. Under similar conditions, phenoxyacetaldehyde is produced in 72% yield from phenoxyacetyl chloride and anisaldehyde from anisyl chloride in 81% yield. Cinnamyl chloride is preferably treated with hydrogen under diminished pressure, whereby cinnamaldehyde is formed, the yield being in the most favourable cases 60% of that theoretically possible;  $\beta$ -phenylpropaldehyde does not appear to be formed to an appreciable extent. *o*-Chlorocinnamic acid is converted by thionyl chloride into *o*-chlorocinnamoyl chloride, b. p.  $153$ – $160^\circ/12$  mm., m. p.  $40^\circ$  (corresponding *anilide*, m. p.  $176^\circ$ ), which is transformed further into *o*-chlorocinnamaldehyde, colourless needles, m. p.  $150^\circ$  (*oxime*, needles, m. p.  $96^\circ$  after softening at  $92^\circ$ ; *acetate* of *oxime*, m. p.  $71$ – $72^\circ$ ). The aldehyde is also prepared by the condensation of *o*-chlorobenzaldehyde with acetaldehyde in the presence of diethylamine. Reduction of the

oxime with sodium amalgam in the presence of glacial acetic acid gives  $\gamma$ -*o*-chlorophenyl-*n*-propylamine which is isolated as the *hydrochloride*, m. p. 167°.

*Salicyloxyacetyl dichloride*, b. p. 174°/17 mm., m. p. 60° (corresponding *anilide*, m. p. 171—172°), could not be reduced in a satisfactory manner. H. W.

**Preparation of Nucleus-halogenated Di(dichloromethyl) Benzenes and Dichloromethyltrichloromethylbenzenes.** LEOPOLD CASSELLA & Co., (D.R.-P. 360414; from *Chem. Zentr.*, 1923, ii, 406).—*o*-, *m*-, and *p*-Xylenes are first chlorinated in the nucleus at low temperatures and in darkness, and then in the side-chain at higher temperatures (120—130°) in light. The products give, on heating with strong sulphuric acid, dialdehydes and aldehyde carboxylic acids. *Dichloro-1:3-di(dichloromethyl)benzene*,  $C_6H_2Cl_2(CHCl_2)_2$ , is a colourless liquid, b. p. 312—313°/760 mm., obtained from dichloro-*m*-xylene. By the action of strong sulphuric acid at 90—100°, *dichloroisophthalaldehyde*,  $C_6H_2Cl_2(CHO)_2$ , crystals, m. p. 145°, is obtained. *Trichloro-1:3-di(dichloromethyl)benzene*,  $C_6HCl_3(CHCl_2)_2$ , is a colourless liquid, b. p. 330—331°/760 mm. It gives with strong sulphuric acid *trichloroisophthalaldehyde*,  $C_6HCl_3(CHO)_2$ , crystals, m. p. 172°. Other compounds mentioned are: *Tetrachloro-1:3-di(dichloromethyl)benzene*, crystals, m. p. 83°; b. p. 359—360°/760 mm.; *tetrachloroisophthalaldehyde*, crystals, m. p. 197°; *chloro-1:3-di(dichloromethyl)benzene*, b. p. 291—292°/760 mm.; *chloroisophthalaldehyde*, m. p. 119°; *dichloro-1:4-di(dichloromethyl)benzene*, b. p. 313—316°/760 mm.; *dichloroterephthalaldehyde*, m. p. 150°; *trichloro-1:2-di(dichloromethyl)benzene*, b. p. 322—324°/760 mm.; *trichlorophthalaldehyde*, m. p. 152°; *trichloro-1:4-di(dichloromethyl)benzene*, b. p. 331—333°/760 mm.; *trichloroterephthalaldehyde*, m. p. 178°; *2:3:5:6-tetrachloro-1:4-di(dichloromethyl)benzene*, b. p. above 360°, m. p. 168°; *2:3:5:6-tetrachloroterephthalaldehyde*, m. p. 200°; *dichloro-1:di-chloromethyl-3-trichloromethylbenzene*, b. p. 321—322°/760 mm.; *dichlorobenzaldehyde-m-carboxylic acid*, nacreous leaflets, m. p. 160°; *trichloro-1-dichloromethyl-3-trichloromethylbenzene*, a thick, colourless oil, b. p. 339—340°/760 mm.; *trichlorobenzaldehyde-m-carboxylic acid*, leaflets, m. p. 214°; *dichloro-1-dichloromethyl-4-trichloromethylbenzene*, b. p. 322—324°/760 mm.; *dichlorobenzaldehyde-p-carboxylic acid*, m. p. 185°; *trichloro-1-dichloromethyl-4-trichloromethylbenzene*, m. p. 120°; *trichlorobenzaldehyde-p-carboxylic acid*, m. p. 216°. G. W. R.

**Decomposition of Aromatic Ketones.** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1923, [iv], 33, 632—637).—The decomposition of aromatic ketones in contact with copper turnings at 550—600° takes place in a manner identical with that of aliphatic ketones (cf. A., 1922, i, 985), scission into three fragments occurring, with formation of carbon monoxide and the two residues attached to it. The aromatic residue by reaction with hydrogen is liberated as an aromatic hydrocarbon, whilst the alkyl group by loss of hydrogen is resolved into an unsaturated hydrocarbon and a

certain quantity of methane. Certain of the ketones studied showed considerable stability and were recovered almost unchanged. This was particularly the case where the ketonic group was attached directly to the nucleus, as, for example, in the case of acetophenone and benzophenone. On the other hand, decomposition occurred with much greater facility with ketones in which the aromatic nucleus was separated from the ketonic group by one or more methylene groups, as in benzyl methyl ketone, cinnamyl ethyl ketone, or dibenzyl ketone.

G. F. M.

**Witt's Method of Diazotisation.** WALTER FUCHS (*Rec. trav. chim.*, 1923, 42, 511—512).—Commenting on a recent paper by Elion (this vol., i, 390), who claimed that Witt's process of diazotisation (addition of a mixture of a base and potassium metabisulphite to nitric acid) did not proceed uniformly but gave nitro-derivatives as by-products, Fuchs points out that Elion used too great an excess of nitric acid. In the case, for instance, of the preparation of 3:5-dibromoacetophenone from 4-amino-3:5-acetophenone, Elion obtained only a 70% yield and about 30% of a nitrated by-product, whereas by using only about one-fifth of the amount of nitric acid the yield of the dibromoacetophenone is practically quantitative.

F. A. M.

**Witt's Method of Diazotisation.** L. ELION (*Rec. trav. chim.*, 1923, 42, 513—515; cf. preceding abstract).—A reply to Fuchs's criticisms. The author denies that the relative amount of nitric acid used is a decisive factor, but emphasises the importance of the concentration of the acid. Thus, if 3:5-dibromo-4-aminobenzoic acid is treated with nitric acid (*d* 1.40) no action occurs, but if the experiment be repeated with acid of *d* 1.48 there is an immediate violent evolution of carbon dioxide, the carboxyl being replaced by a nitro-group. This also occurs even in the presence of potassium metabisulphite. In the same way, 3:5-dibromo-4-aminoacetophenone is also readily converted into the same 3:5-dibromo-1-nitro-4-aminobenzene, but of course without evolution of carbon dioxide. Elion disputes Fuchs's claim to have obtained quantitative yields of nitrogen-free product from 3:5-dibromo-4-aminoacetophenone by Witt's method.

F. A. M.

**Action of Alcoholic Potassium Hydroxide on Ketones.**  
VIII. The Replacement of Bromine by Hydrogen in Bromobenzophenones and their Derivatives. P. J. MONTAGNE (*Rec. trav. chim.*, 1923, 42, 499—510; cf. A., 1920, i, 394; this vol., i, 227).—Previous work has shown that when 2-bromobenzophenone is heated with alcoholic potassium hydroxide benzhydrol is formed, but with 3- and 4-bromobenzophenones the bromine atoms are practically unattacked, the products being respectively 3- and 4-bromobenzhydrols (cf. A., 1913, i, 55). Again, with 3:5-dibromobenzophenone the CO-group is reduced but the bromine is only partly replaced. It has now been found that 3:5-dibromo-4-hydroxybenzophenone remains unaltered when heated with alcoholic potash and 2'-bromo-4-hydroxybenzophenone (prepared by

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boiling 2-bromo-4-ethoxybenzophenone with acetic and hydrobromic acids as colourless crystals, m. p.  $114^{\circ}$ , b. p.  $260^{\circ}/10$  mm.) was only slightly attacked by hot alcoholic potash.

On treating 3:5-dibromo-4-aminobenzophenone for two days with alcoholic potash, two products were obtained: 3:5-dibromo-4-aminobenzhydrol (m. p.  $149.5^{\circ}$ ) and 3-bromo-4-aminobenzophenone. 4-Aminobenzophenone remained unchanged after four days' treatment, as also did 3-bromo-4-aminobenzophenone after two days (prepared by brominating aminobenzophenone in acetic acid as colourless crystals, m. p.  $157-158^{\circ}$ , b. p.  $241^{\circ}/11$  mm.). 3:5-Dibromo-4-aminobenzhydrol is unattacked by hot alcoholic potash.

F. A. M.

**The Formation of Six-membered Carbon Rings.** FRITZ MAYER and GEORG STAMM (*Ber.*, 1923, 56, [B], 1424-1433).—The formation of six-membered carbon rings by the action of aluminium chloride on  $\gamma$ -phenyl-*n*-butyryl chloride and its homologues formed by the introduction of methyl groups into the nucleus or side chain has been investigated. With the parent substance, the yield of ketone is only 10% of that theoretically possible, whereas when a methyl group is present in very varied position the yield rises to between 70% and 76%.

Methylsuccinic acid is obtained conveniently in 93% yield by the hydrogenation under somewhat increased pressure of citraconic anhydride dissolved in water in the presence of palladous chloride and animal charcoal.

The requisite acid chlorides are obtained by the interaction of the acids at the atmospheric temperature with thionyl chloride which is purified by two distillations followed by distillation from quinoline and finally from linseed oil. They are allowed to react with aluminium chloride in the presence of light petroleum, b. p.  $70-80^{\circ}$ , which has been purified by agitation with fuming sulphuric acid (containing about 20%  $\text{SO}_3$ ), then with water, followed by desiccation with calcium chloride and distillation over sodium.

Phenylbutyryl chloride gives 1-keto-1:2:3:4-tetrahydronaphthalene, b. p.  $133-135^{\circ}/14$  mm. 1-Keto-7-methyl-1:2:3:4-tetrahydronaphthalene, b. p.  $143-145^{\circ}/15$  mm., m. p.  $35-36^{\circ}$  (semicarbazone, m. p.  $226-228^{\circ}$ ), is obtained in 72% yield from  $\gamma$ -*p*-tolyl-*n*-butyryl chloride.

The action of benzene on methylsuccinic anhydride leads to the production of a mixture of  $\beta$ -benzoyl- $\alpha$ -methylpropionic acid, m. p.  $139-140^{\circ}$ , and  $\beta$ -benzoyl- $\beta$ -methylpropionic acid, m. p.  $56-59^{\circ}$  after previous softening. The former acid is transformed by Clemmensen's method into  $\gamma$ -phenyl- $\alpha$ -methyl-*n*-butyric acid, which is converted into 1-keto-2-methyl-1:2:3:4-tetrahydronaphthalene, b. p.  $135-137^{\circ}/16$  mm. (semicarbazone, m. p.  $200-201^{\circ}$ ), in 70% yield. In a similar manner, methylsuccinic anhydride and toluene in the presence of aluminium chloride give a mixture of  $\beta$ -*p*-toluoyl- $\alpha$ -methylpropionic acid, colourless leaflets, m. p.  $169-171^{\circ}$  [oxime, slender, colourless needles, m. p.  $141-142^{\circ}$  (decomp.)], and  $\beta$ -*p*-toluoyl-*n*-butyric acid, m. p.  $63-65^{\circ}$  (oxime, m. p.  $139-$

141°). The constitution of the former acid is established by its syntheses from *p*-tolyl bromomethyl ketone and ethyl isosuccinate in the presence of sodium and alcohol.  $\gamma$ -*p*-Tolyl- $\alpha$ -methyl-*n*-butyric acid, m. p. 54–55°, b. p. 183–184°/15 mm. (ethyl ester, b. p. 149–151°/14 mm.), is obtained from the corresponding toluoyl acid by the action of amalgamated zinc and hydrochloric acid. The corresponding chloride has b. p. 145–146°/15 mm, and the amide has m. p. 150–151°. The chloride gives 1-*keto*-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 145–147°/15 mm. (semicarbazone, m. p. 220–221°), the yield being 75% of that theoretically possible.  $\beta$ -*p*-Toluoyl-*n*-butyric acid is transformed successively into ethyl  $\gamma$ -*p*-tolyl- $\beta$ -methyl-*n*-butyrate, b. p. 149–151°/14 mm.;  $\gamma$ -*p*-tolyl- $\beta$ -methyl-*n*-butyric acid, b. p. 180–181°/15 mm.;  $\gamma$ -*p*-tolyl- $\beta$ -methyl-*n*-butyryl chloride, b. p. 141–143°/15 mm., and 1-*keto*-3 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 150°/15 mm., m. p. 52–53° (semicarbazone, m. p. 203–205°).

$\gamma$ -Phenyl- $\Delta^8$ -butenoic acid, colourless leaflets, m. p. 75–78°, prepared from ethyl  $\beta$ -benzoylpropionate and magnesium methyl iodide, is catalytically hydrogenated in the form of its sodium salt to  $\gamma$ -phenylvaleric acid, b. p. 169–170°/14 mm., the chloride of which is transformed into 1-*keto*-4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 145–160° (semicarbazone, colourless leaflets, m. p. 210°). In a similar manner,  $\gamma$ -*p*-tolylvaleric acid, b. p. 178–180°/15 mm., is converted successively into the chloride, b. p. 145–155°/16 mm., and 1-*keto*-4 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 145–152°/15 mm. (semicarbazone, colourless leaflets, m. p. 194–195°).

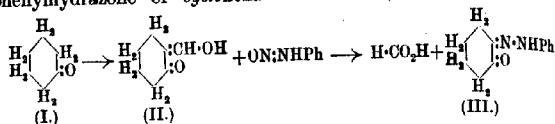
The condensation of citraconic anhydride with benzene in the presence of aluminium chloride leads to the formation of small yields of a mixture of  $\beta$ -benzoyl- $\alpha$ -methylacrylic acid, colourless needles, m. p. 150° after softening at 120° (the acid is identified by its hydrogenation to  $\beta$ -benzoyl- $\alpha$ -methylpropionic acid) and  $\beta$ -benzoyl- $\Delta^8$ -butenoic acid, slender needles, m. p. 100–102° after softening at 80°. In a similar manner, toluene and citraconic anhydride yield  $\beta$ -*p*-toluoyl- $\alpha$ -methylacrylic acid, m. p. 138–139°, and  $\beta$ -*p*-toluoyl- $\Delta^8$ -butenoic acid, colourless leaflets, m. p. 94–95°; the constitutions of these acids are established by their reduction to the corresponding saturated acids.

H. W.

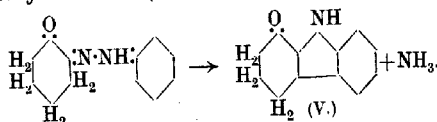
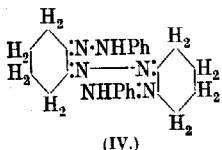
The Isomerism of the Oximes. XII. Hydrochlorides. OSCAR LISLE BRADY and FREDERICK PERCY DUNN (T., 1923, 123, 1783–1803).

Derivatives of cycloHexan-1 : 2-dione. SAMUEL COFFEY (Rec. trav. chim., 1923, 42, 528–532).—Attempts to prepare cyclohexanedione by condensing cyclohexanone in large excess with aldehydes gave in all cases well crystallised, yellow 2 : 6-dibenzylidene derivatives, of which the following are new : 2 : 6-dipiperonylidene cyclohexanone, m. p. 187–188°; 2 : 6-di-*m*-nitrobenzylidene cyclohexanone, lustrous, golden needles, m. p. 191–192°; 2 : 6-di-*ansyl*idene cyclohexanone, which melts at 162° to a turbid, anisotropic liquid showing the characteristic properties of liquid crystals

and clearing sharply at 172°. The monophenylhydrazone of *cyclohexan-1:2-dione* was made in the following manner: *cyclohexanone* (I) and amyl formate were condensed together by Borsche's method (A., 1910, i, 880) to give *hydroxymethylenecyclohexan-1:2-one* (II) which condensed with diazotised aniline to give the monophenylhydrazone of *cyclohexan-1:2-dione* (formula III), which



forms lustrous, reddish-brown scales, m. p. 183—185°. It is sparingly soluble in most organic solvents. Further treatment with phenylhydrazine yielded the osazone of *cyclohexan-1:2-dione*, forming long, yellow needles, m. p. 153—154°, which had been obtained by Kötze (A., 1913, i, 1201) by the action of phenylhydrazine on 2-hydroxycyclohexanone. With hydrazine hydrate, the monophenylhydrazone gave a colourless, unstable, oily product, probably the hydrazone-phenylhydrazine of the diketone. On the addition of a little dilute acetic acid, a crimson precipitate was at once produced consisting of the ketazine (*cyclohexandione-ketazine-2:2'-diphenylhydrazone*) (IV). Treatment of the monophenylhydrazone of *cyclohexandione* with a mixture of acetic and hydrochloric acids led to the formation not of the free diketone but of 1-ketotetrahydrocarbazole (formula V) by Fischer's indole synthesis,



After recrystallisation from 50% alcohol or acetic acid, the substance formed flat needles several cm. long, m. p. 169—170°; it is stable to dilute acids and alkalis, and could not be acetylated or benzoylated. The *phenylhydrazone* is oily and unstable, and the *oxime* was obtained as a glassy mass. The *semicarbazide* formed crystals melting at about 228—230°. On heating with alcoholic hydrazine hydrate, the lemon-yellow *ketazine*,  $\text{C}_{24}\text{H}_{22}\text{N}_4$ , m. p. 258—260°, was formed; it is sparingly soluble in most common solvents. F. A. M.

**The Dibenzoylxylenes and Dinaphthanthracenediquinones.** HENRI DE DIESBACH [with WERNER PERRIG, MELCHIOR BETSCHART, and KARL STREBEL] (*Helv. Chim. Acta*, 1923, 6, 539—548).—A new synthesis of linear dinaphthanthracenediquinone is described which consists in condensing the acid chloride of  $\alpha$ - or  $\beta$ -cumidic acid with benzene to obtain dibenzoylxylenes, oxidising the methyl groups to carboxyl groups, and heating with sulphuric acid to form

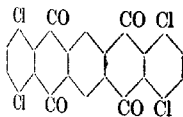
the diquinone. New syntheses of  $\alpha$ - and  $\beta$ -cumidic acids are described. By heating 2:5-dibromo-*p*-xylene with cuprous cyanide and pyridine in an autoclave at 200° for eight hours, 2:5-dicyano-*p*-xylene was obtained, colourless needles, m. p. 209.5–210°. It is converted quantitatively by boiling 70% sulphuric acid into  $\beta$ -cumidic acid.  $\beta$ -Cumidoyl chloride forms long needles, m. p. 116°. 4:6-Dibromo-*m*-xylene, when heated in the same manner with cuprous cyanide, gives 4:6-dicyano-*m*-xylene, crystallising in long, colourless needles, m. p. 144–145°, which is readily hydrolysed to  $\alpha$ -cumidic acid. When the crude chloride of this acid is heated with benzene and aluminium chloride, 4:6-dibenzoyl-*m*-xylene is formed, colourless needles, m. p. 104°. At the same time, there is formed 5-benzoyl-2:4-dimethylbenzoic acid, crystallising in small prisms, m. p. 149–150°. Instead of benzene, *p*-dichlorobenzene can be condensed with  $\alpha$ -cumidoyl chloride, when there is formed 4:6-di(2':5'-dichlorobenzoyl)-*m*-xylene, colourless needles, m. p. 133–134°, and at the same time 5(2':5'-dichlorobenzoyl)-2:4-dimethylbenzoic acid, m. p. 180°. With *p*-dimethoxybenzene,  $\alpha$ -cumidoyl chloride condenses to form 4:6-di(2'-hydroxy-5'-methoxybenzoyl)-*m*-xylene, long, greenish-yellow prisms or needles, m. p. 139–140°. During this condensation, two methoxy-groups are hydrolysed.

$\beta$ -Cumidoyl chloride condenses with benzene in presence of aluminium chloride, forming 2:5-dibenzoyl-*p*-xylene, hexagonal prisms, m. p. 160°, and 4-benzoyl-2:5-dimethylbenzoic acid, colourless, prismatic needles, m. p. 151–152°. The diketones prepared from  $\beta$ -cumidic acid are less soluble and more difficult to burn than those from  $\alpha$ -cumidic acid. 2:5-Di(2':5'-dichlorobenzoyl)-*p*-xylene crystallises in spangles, m. p. 182°, and 4(2':5'-dichlorobenzoyl)-2:5-dimethylbenzoic acid forms small prisms, m. p. 193°. When condensed with toluene,  $\beta$ -cumidoyl chloride gives 2:5-di-*p*-toluoyl-*p*-xylene, colourless prisms, m. p. 162°, and with anisole, 2:5-di-*p*-anisoyl-*p*-xylene, colourless prisms, m. p. 177°.

The above diketones are oxidised by nitric acid (*d* 1.15), at 200°, to dibenzoylbenzenedicarboxylic acids. Thus 4:6-dibenzoyl-*m*-xylene gives the known 4:6-dibenzoylisophthalic acid, and 2:5-dibenzoyl-*p*-xylene gives 2:5-dibenzoyltetraphthalic acid, and these are readily converted into dinaphthanthracediquinone (cf. Philippi, A., 1911, i, 793). By oxidising 4:6-di(2':5'-dichlorobenzoyl)-*m*-xylene, 4:6-di(2':5'-dichlorobenzoyl)isophthalic acid was obtained, crystallising in spangles, m. p. 264–266° (decomp.). Its dimethyl ester forms a crystalline powder, m. p. 178°. When the acid is heated with sulphuric acid monohydrate it is converted into 1:4:8:11-tetrachloro-5:7:12:14-dinaphthanthracediquinone (annexed formula), crystallising in greenish-yellow needles, decomposing at about 340°. It forms a violet-blue hydro-

sulphite vat, but the sodium salt of the reduction product is almost insoluble, and, unlike the unsubstituted diphthaloylbenzene, does not oxidise in air.

E. H. R.



**Purpurogallin.** J. HERZIG (*Annalen*, 1923, 432, 99—114).—The action of ethyl-alcoholic potash on tetramethylpurpurogallin gives a *trimethylethylpurpurogallin*, m. p. 114—116°, the reverse change not being effected by means of methyl-alcoholic potassium hydroxide. A second *trimethylethylpurpurogallin*, m. p. 105—107°, is produced by the action of alkali and ethyl sulphate on trimethylpurpurogallin. Warm concentrated sulphuric acid converts trimethylpurpurogallin or tetramethylpurpurogallin into *dimethylpurpurogallin*, orange-red needles, m. p. 193—195°, which gives a *diacetate*, white crystals, m. p. 180—181°. The trimethylethyl ether, m. p. 114—116°, gives a *monomethylpurpurogallin*, m. p. 193—194°, whilst the isomeric ether, m. p. 105—107°, gives a mixture, m. p. 158—162°, of monomethyl ether and dimethyl ether. The action of diazomethane on this mixture, on the dimethyl ether, m. p. 193—195°, or on the monomethyl ether, m. p. 193—194°, gives the same trimethylpurpurogallin, m. p. 179° (Perkin and Steven, T., 1903, 83, 196). It is concluded that purpurogallin, as distinct from any possible isomeride, is the parent substance of all the above-mentioned compounds.

The alkaline reduction of tetramethylgalloflavin gives an amorphous substance in the formation of which one methoxyl has become hydrolysed, which contains the free hydroxyl and carboxyl groups which form the lactone ring in *isogalloflavin*. Trimethylpurpurogallin behaves similarly when reduced by means of alkali hydroxide and zinc dust, giving an amorphous product, which has not been obtained pure, but which is certainly a dimethyl ether; it is converted by means of diazomethane into a compound having a methoxyl content corresponding with the trimethyl ether. Similarly, the dimethyl ether, m. p. 193—195°, is converted into a monomethyl ether, which likewise gives a trimethyl derivative with diazomethane.

When air is led through a dilute alkaline solution of purpurogallin, a green coloration appears, but eventually gives place to a reddish-brown shade. A pure product has not, however, been isolated from this experiment (but cf. Perkin and Steven, *loc. cit.*). W. S. N.

**The Phenanthrene Series. XXXIV. The Preparation of 2-Hydroxymorpholquinone [2:3:4-Trihydroxyphenanthraquinone] from 4-Nitrophenanthraquinone.** JULIUS SCHMIDT and OTTO SCHAIRER (*Ber.*, 1923, 56, [B], 1331—1337).—3:4-Dihydroxyphenanthraquinone is the only product of the degradation of the opium alkaloids which has been obtained from phenanthraquinone, but its preparation is not easy owing to difficulties in the preparation of 3-nitrophenanthraquinone (cf. Schmidt and Söll, A., 1908, i, 995). In the hope of ultimately obtaining morpholquinone or a derivative thereof more readily, the preparation of 4-nitrophenanthraquinone (Schmidt and Austin, A., 1904, i, 69) has been re-examined without thereby effecting any improvement in the method. 2:3:4-Trihydroxyphenanthraquinone has, however, been obtained in small yield from 4-hydroxyphenanthraquinone.

Phenanthraquinyl monoacetate crystallises in almost colourless,

matted needles, m. p. 181—182° [Goldschmidt and Schmidt (A., 1922, i, 1149) gave m. p. 170° (decomp.)]; it is readily converted by boiling acetic anhydride into phenanthraquinyl diacetate, m. p. 202°. Under widely varied conditions, neither of the substances could be converted by nitric acid into 4-nitrophenanthraquinone. 2:7-Dinitro-9:10-diacetoxyphenanthrene, m. p. about 280° (decomp.), can, however, be readily prepared by the action of nitric acid (*d* 1.45) on the diacetate in the presence of acetic acid and acetic anhydride.

2:3-Dinitro-4-hydroxyphenanthraquinone, pale red, crystalline leaflets, m. p. 248° (decomp.), is obtained by the action of nitric acid on 4-hydroxyphenanthraquinone, only small quantities of which should be taken for each experiment. The corresponding acetate forms reddish-brown crystals, m. p. 233° (decomp.); the monoxime, orange-coloured crystals, decomp. 214—215°, is described. The hydroxy-compound is conveniently identified by converting it into 2:3-dinitro-4-hydroxyphenanthraquinone,  $\text{HO} \cdot \text{C}_6\text{H}(\text{NO}_2)_2 \cdot \text{C} \cdot \text{N} > \text{C}_6\text{H}_4$ , slender, pale brown needles, m. p.

240° (decomp.). The constitution of 2:3-dinitro-4-hydroxyphenanthraquinone is established by its oxidation by potassium dichromate and sulphuric acid to phthalic acid from which it follows that the three substituents are attached to the same benzenoid nucleus; the presence of the nitro-groups in the 2:3-position is deduced as a result of the authors' experience that the nitro-group never enters in position 1. The dinitro-compound is reduced by tin and hydrochloric acid to 2:3-diamino-4-hydroxyphenanthraquinone, which is diazotised with some difficulty and subsequently converted into 2:3:4-trihydroxyphenanthraquinone, a brownish-red powder, m. p. 185°, in small yield. 2:3:4-Trihydroxyphenanthraquinone forms small, brown crystals, m. p. about 255° (decomp.).

H. W.

**A New Class of Free Organic Radicles. IV. ROLAND SCHOLL, HEINRICH DEHNERT, and HANS SEMP (Ber., 1923, 56, [B], 1633—1638).**—Knowledge of the 1-aryloxanthronyls has been gained previously mainly as a result of experiments with 1-*p*-chlorobenzoyloxanthronyl. In the present communication the preparation of a series of 1-arylanthraquinones and their conversion into 1-aryloxanthronyls are described.

1-Arylanthraquinones are obtained from anthraquinone-1-carboxyl chloride by the Friedel-Crafts method. The formation of blue by-products, undoubtedly oxanthronyls, is invariably observed, and is attributed to the dehydrogenating action of anhydrous aluminium chloride on aromatic nuclei in which the anthraquinone-1-carboxyl chloride functions as catalyst. The formation of the blue substances is favoured by increasing mobility of the hydrogen atoms of the aromatic compound which is used and by rise in temperature during the reaction. The most favourable conditions for the production of the ketones are obtained when carbon disulphide is used as solvent and the temperature is kept as low as

possible. The oxanthronyls are obtained by reducing the 1-aryl anthraquinones with zinc dust and glacial acetic acid to 1-aryl anthraquinols and disproportionation or dehydrogenation of the latter by hydrochloric acid.

The following individual substances are described: *m*-xylyl 1-anthraquinonyl ketone,  $C_6H_4(CO)_2C_6H_3-CO-C_6H_2Me_3$ , prisms, capped by pyramids, m. p. 191–192°; 1-anisoylanthraquinone, m. p. 205° (Schaarschmidt, A., 1915, i, 566, gives m. p. 269°); *p*-di-phenylyl 1-anthraquinonyl ketone,  $C_6H_4(CO)_2C_6H_3-CO-C_6H_4Ph$ , small, pale yellow needles, m. p. 234°.

$C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ \diagdown C \diagup \\ | OH \end{array} C_6H_3 \cdot C \cdot Ph$  1-benzoyl-9-oxanthronyl (annexed formula), bluish-violet needles with copper reflex, m. p. 192–193°; 1-*p*-toluoyl-9-oxanthronyl, m. p. 182–183°; 1-*m*-xyloyl-9-oxanthronyl, dark violet-blue, metallic needles, m. p. 171–172°; 1-anisoyl-9-oxanthronyl, needles, m. p. 167–168°; 1-*p*-phenylbenzoyl-9-oxanthronyl, m. p. 216–217°; 1- $\alpha$ -naphthoyl-9-oxanthronyl, m. p. 198–199°.

Internally complex hydroketyls have also been obtained in the naphthalene series.

H. W.

**Preparation of Inactive Menthol.** RHEINISCHE KAMPFER-FABRIK G. M. B. H. (Brit. Pat. 189450).—By treatment with hydrogen at 5–30 atmospheres and 200° in presence of finely divided nickel, cobalt, platinum, or palladium, thymol yields a mixture of inactive menthol and liquid isomenthol. The latter is dehydrogenated to menthone by heating at 200° with copper oxide in presence of alkali, and the menthone hydrogenised to inactive menthol in the same manner as thymol.

T. S. W.

**$\pi$ -Chlorosulphoxidecamphor and *iso*Ketopinic Acid [Nor- $\pi$ -camphor-7-carboxylic Acid].** E. WEDEKIND and R. STÜSSER (Ber., 1923, 56, [B], 1557–1561; cf. Wedekind, Schenk, and Stüsser, this vol., i, 346).—In the previous communication, the conversion of Reyher's acid into 10-chlorosulphoxidecamphor has been described and the hypothesis has been put forward that the process is applicable to all sulphonyl chlorides in which the sulphonyl residue is present in a methyl group. Confirmation of this view is found in the behaviour of  $\pi$ -camphorsulphonic acid.

$\pi$ -Chlorosulphoxidecamphor (annexed formula), m. p. about 190° (decomp.), is prepared by the action of pyridine on  $\pi$ -camphorsulphonyl chloride; it gives a normal phenylhydrazone, small, yellow needles, m. p. 167–168°. It is oxidised by potassium permanganate in alkaline solution to *isoketopinic acid* (nor- $\pi$ -camphor-7-carboxylic acid) (annexed formula), m. p. 245°, which can also be prepared by means of nitric acid (*d* 1.34); the corresponding phenylhydrazone has m. p. 200° (decomp.).

Attempts to sulphonate other cyclic ketones by Reyher's method are also described; menthone and fenchone

are, however, almost unaffected, whilst cyclohexanone and carvone do not yield crystalline sulphonic acids.

Fluorene is transformed by sulphuric acid and acetic anhydride quantitatively into fluorene-2-sulphonic acid in place of the desired fluorene-9-sulphonic acid. On the other hand, sodium fluorene-9-sulphonate can be prepared in small yield by the action of boiling, concentrated sodium hydrogen sulphite solution on 9-chlorofluorene. Attempts to transform the salt by means of phosphorus pentachloride into fluorene-9-sulphonyl chloride were not successful, since the drastic conditions necessary for the change cause the primarily formed chloride to decompose with evolution of sulphur dioxide and production of 9-chlorofluorene. H. W.

#### Preparation of Basic Derivatives of Camphorimide.

MARGARET FREIFRAU VON AXTER (D.R.-P. 362379; from *Chem. Zentr.*, 1923, ii, 480—481).—The imido-hydrogen of camphorimide is replaced by basic groups of the composition  $\text{C}_n\text{H}_{2n}\text{NRR}'$  (where R=alkyl or hydrogen and R'=alkyl). These basic compounds may be obtained by treating camphorimide in the presence of sodium ethoxide with halogen substituted bases such as chlorotriethylamine,  $\text{NEt}_2\text{C}_2\text{H}_4\text{Cl}$ , or by treating halogen alkyl imides of camphoric acid of the composition  $\text{C}_8\text{H}_{14}\text{CO}_2\text{N}\cdot\text{C}_n\text{H}_{2n}\text{X}$

with primary or secondary amines, or by heating camphoric acid (or its anhydride) with *as*-dialkylated diamines of the composition  $\text{NH}_2\text{C}_n\text{H}_{2n}\text{NRR}'$ , or camphor dialkylaminoalkylamidic acids are changed into basic imides by way of  $\alpha$ - or  $\beta$ -camphor isodialkylaminoalkylamides of the composition  $\text{C}_8\text{H}_{14}\text{CO}_2\text{N}\cdot\text{C}_n\text{H}_{2n}\text{NRR}'$ .

Camphor- $\beta$ -diethylaminoethylimide,  $\text{C}_8\text{H}_{14}\text{CO}_2\text{N}\cdot\text{C}_2\text{H}_5\cdot\text{NEt}_2$ , forms blunt needles, m. p. 87—88°. The hydrochloride has m. p. 11—93°. It is prepared by the action of chlorotriethylamine on camphorimide or of *as*-diethylethylenediamine on camphoric anhydride, or by heating camphor- $\beta$ -diethylaminoethylamidic acid,  $\text{HO}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_5\cdot\text{NEt}_2$ , or by heating camphor- $\beta$ -bromoethylimide with diethylamine at 100—120°. Camphordiethylaminoethylamidic acid is obtained by gentle heating of a solution of camphoric anhydride and diethylethylenediamine in benzene; it forms needles in star-shaped clusters, m. p. 172—173° (decomp.). Camphor- $\beta$ -bromoethylimide is a viscid, colourless oil, b. p. 185—190°/12 mm.; it is prepared by the action of ethylene bromide on camphorimide. When heated in alcoholic or benzene solution with methylamine, it gives camphor- $\beta$ -methylaminoethylimide,  $\text{C}_8\text{H}_{14}\text{CO}_2\text{N}\cdot\text{C}_2\text{H}_5\cdot\text{NHMe}$ , a basic oil (cf. A., 1922, i, 254).

G. W. R.

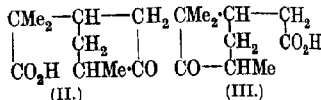
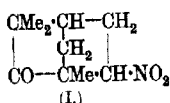
**Preparation of Methylenecamphor.** HANS RUPE and ALTER KUSSMAUL (Swiss Pat. 87757; from *Chem. Zentr.*, 1923, 527).—Camphylcarbinol is heated with 70—80% sulphuric

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acid, for example, at 100°. The products of reaction are then poured on to ice and extracted with ether. The reaction proceeds according to the equation  $C_8H_{14} \begin{smallmatrix} \diagup CH \cdot CH_2 \cdot OH \\ \diagdown CO \end{smallmatrix} = C_8H_{14} \begin{smallmatrix} \diagup C \cdot CH_2 \cdot \\ \diagdown CO \end{smallmatrix} + H_2O$ . *Methylenecamphor* is obtained after removal of the ether by distillation as a white, wax-like mass with a strong odour of camphor; it has m. p. 43.5–44°, and b. p. 82–84°/10 mm.

G. W. R.

**The Action of Nitric Acid on Fenchone.** S. S. NAMETKIN [with (MLLE) K. D. LUBOVCOVA and (MLLE) V. A. CHOCHRIAKOVA] (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 169–176).—By the action of dilute nitric acid on fenchone, Konovalov (A., 1904, i, 257) prepared, in addition to the well-known tertiary-4-nitrofenchone, a secondary nitrofenchone, m. p. 88°,  $[\alpha]_D -42.88^\circ$ ; and it is now shown that these substances are also accompanied by isocamphoronic and  $\alpha$ -dimethyltricarballic acids, both of which Gardner and Cockburn (T., 1898, **73**, 708) have obtained by the oxidation of fenchone by means of nitric acid. Now isocamphoronic acid is doubtless produced by the further degradation of the secondary nitrofenchone and for this reason the formula (I) is assigned to this substance.



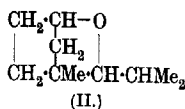
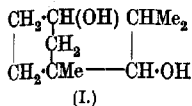
(III.)

The nitroketone is shown to be analogous to  $\alpha$ -nitrocamphor (Lowry, T., 1898, **73**, 986; 1903, **83**, 953) in its behaviour towards ferric chloride and permanganate and it is concluded that it is a true nitro-compound. The action of bromine on a solution of the nitroketone in alkali leads to a *bromonitrofenchone*,  $C_{10}H_{14}O_3NBr$ , forming colourless plates from alcohol, m. p. 53°, stable to heat in the presence of an indifferent solvent. On reduction with zinc and acetic acid, or tin and hydrochloric acid, the nitro-ketone passes into a *keto-acid*,  $C_{10}H_{16}O_3$ , which is probably a mixture of stereoisomerides, because it has no sharp melting point (73–76°, clears 79–80°); the *semicarbazone* decomposes without melting at 188°. The structure of the acid is most probably represented by formula (II) although the alternative formula (III) is also possible.

G. A. R. K.

**Konovalov's "Hydroxyfenchone."** II. S. S. NAMETKIN and (MLLE) V. A. CHOCHRIAKOVA (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 163–168; cf. A., 1916, i, 217).—It has already been shown (*loc. cit.*) that the compound  $C_{10}H_{16}O_2$  obtained by Konovalov (A., 1904, i, 257) by the reduction of 4-nitrofenchone is a monocyclic diketone, formed by the fission of one ring in the bicyclic system present in fenchone. It is now shown that on reduction the diketone passes into a *glycol*, b. p. 151–152°/11 mm.,

$[\alpha]_D +44.54^\circ$  (*acetyl* derivative, oil, b. p.  $152-153^\circ/12$  mm.,  $n_D^{20}$  1.4630,  $d_4^{20}$  1.0189); the glycol very readily passes into an *oxide* when dehydrated with dilute sulphuric acid and for this reason the formula (I) is suggested for the glycol, the oxide being represented by (II),

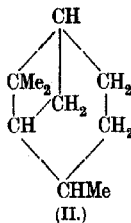
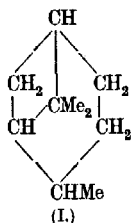


The oxide is a colourless liquid with an odour reminiscent of cineole, b. p.  $171-172^\circ/749$  mm.,  $d_4^{20}$  0.8985,  $n_D^{20}$  1.4478.

It is pointed out that the great stability usually shown by the bicyclic system of fenchone is profoundly affected by the replacement of the tertiary hydrogen atom by a nitro-group, fission readily taking place under the influence of mild reagents; this fission appears to occur in the neighbourhood of the  $\text{-CMe}_2$ -group, as in the splitting of fenchone by the action of sodamide (Semmler, A., 1906, i, 681).

G. A. R. K.

**The Stereochemistry of Alicyclic Compounds. I. Dihydropinenes.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 177-194).—A short account of this work has already appeared (this vol., i, 588). It has been shown that the catalytic reduction of *l*-pinene by a modification of Sabatier and Senderens's method leads to a perfectly individual dihydrocompound which has been named pinane (this vol., i, 692). It is now found that when either *d*-pinene (partly racemised) isolated by careful fractionation from Russian turpentine (b. p.  $154.5-155^\circ$  [corr.],  $d_4^{20}$  0.8597,  $n_D^{20}$  1.4663,  $[\alpha]_D +24.9^\circ$ ) or inactive pinene, prepared by the regeneration of the nitrosochloride of *d*-pinene (Tilden, T., 1904, 85, 763) are similarly hydrogenated, the product consists of a mixture of two hydrocarbons; it boils within a range of several degrees and the physical properties do not agree with those of pinane. The dihydro-compound was then prepared from *d*-pinene by converting the latter into pinocamphone and treating its *hydrazone*, a colourless oil, b. p.  $134-135^\circ/22$  mm.,  $d_4^{20}$  0.9917,  $n_D^{20}$  1.5155, either with potassium hydroxide (Kijner, A., 1911, i, 679), or sodium ethoxide (Wolff, A., 1912, i, 988). The first preparation of the hydrocarbon, *pinocamphane*, had b. p.  $164.5-165^\circ/763$  mm.,  $d_4^{20}$  0.8551,  $n_D^{20}$  1.4609,  $[R_L]_D$  44.33 (calc. 43.98); the second had b. p.  $163.5-164^\circ/747$  mm.,  $d_4^{20}$  0.8558,  $n_D^{20}$  1.4611,  $[R_L]_D$  44.31; pinocamphane is thus an individual hydrocarbon distinct from pinane in its physical properties (cf. *loc. cit.*). It is suggested that both hydrocarbons are normal hydrogenation products of pinene and that a mixture of the two is produced from *d*- or *r*-pinene by the Sabatier-Senderens method. It is shown that two dihydropinenes are possible; corresponding with the *d*- and *l*-forms of pinene and formulated thus:



Actually, formula (I) probably represents pinocamphane and (II) is assigned to pinane, by analogy with isobornylane and fenchane (A., 1916, i, 269); in the latter case the hydrocarbon (fenchane) possessing no substituents on the carbon atom forming the bridge shows an exaltation of the molecular refraction as compared with isobornylane (0.26) and the same difference is observed in the refractions of pinane and pinocamphane.

It is clear that the reduction of either the racemic or optically impure *d*-pinene should lead to a mixture of the two hydrocarbons; the individual *l*-pinene gives only one of them, owing presumably to the selective addition (*cis* or *trans*) of hydrogen to the double linking, such selective additions having been observed in some cases of hydrogenation of triple bonds.

The results obtained by Zelinski (A., 1911, i, 997), who used a higher temperature for the reduction of pinene, are probably attributable to partial isomerisation of the latter. G. A. R. K.

**Action of Phosphorus Pentachloride on Pinene.** LÉONCE BERT (*Bull. Soc. chim.*, 1923, **33**, 787—790).—When phosphorus pentachloride acts on pinene in the cold, hydrogen chloride is liberated and the other products of the reaction are, besides phosphorus trichloride, *p*-cymene (in about 13% yield), an unstable liquid pinene dichloride, a stable solid pinene dichloride, m. p. 183°, a dark yellow resin, and much tarry matter. H. H.

**Curious Case of Separation of Optical Antipodes by Distillation and by Crystallisation.** GEORGES DUPONT and L. DESALBRES (*Compt. rend.*, 1923, **176**, 1881—1884).—In the fractional distillation of various pine oils, inactive pinene distils over in the first fractions. Similarly, on freezing the distillates, active pinene separates, the inactive variety being concentrated in the mother-liquors. The presence of inactive pinene decreases the velocity of crystallisation of the active compound, apparently acting simply as a foreign substance, since no evidence could be obtained for the existence of a racemic compound in the liquid state. No explanation is forthcoming to account for the distillation effect. E. E. T.

**Action of a Saturated Solution of Hydrogen Chloride in Acetic Acid on Oil of Turpentine.** R. HUIERRE (*J. Pharm. Chim.*, 1923, [vii], **27**, 441—448).—When 1 part of turpentine is gradually added to 4 parts of a saturated solution of hydrogen

chloride in glacial acetic acid a reaction occurs which is accompanied by a considerable rise of temperature, and on allowing the reaction product to evaporate spontaneously at a temperature below  $15^{\circ}$  a separation into two layers occurs, the upper layer consisting of a terpene monohydrochloride boiling with slight decomposition between  $150^{\circ}$  and  $200^{\circ}$ , and having  $\alpha_D -10^{\circ}$  in 5% ethyl acetate solution. The hydrogen chloride is very firmly retained in this compound and is only very partly eliminated by aqueous or alcoholic potassium hydroxide, but more readily by sodium acetate and acetic acid. The lower acetic acid layer of the above reaction product on further spontaneous evaporation below  $15^{\circ}$  deposits crystals which were identified as terpin, and were obtained pure and anhydrous by recrystallisation from boiling ethyl acetate.

G. F. M.

**The Preparation of *d*- and *l*-Limonene in the Pure Condition.** JULIUS VON BRAUN and GEORG LEMKE (*Ber.*, 1923, 56, [B], 1562—1563).—The authors' previous experience has shown that bromine atoms attached to vicinal carbon atoms are very readily and smoothly removed by the action of magnesium in the presence of ether. The method has been applied to the isolation of *d*- and *l*-limonene from the corresponding pure tetra-bromides. *d*-Limonene prepared in this manner and finally purified by distillation over sodium has b. p.  $176-176.4^{\circ}$ ,  $n_D^{20}$  0.8411,  $[\alpha]_D^{20} +126^{\circ} 8.4'$  in substance,  $[\alpha]_D^{20} +117^{\circ} 27'$  when dissolved in chloroform. *l*-Limonene has b. p.  $176-176.4^{\circ}$ ,  $n_D^{20}$  0.8422,  $[\alpha]_D^{20} -122^{\circ} 6'$  in substance.

H. W.

**Researches on Phellandrenes.** I. HENRY GEORGE SMITH, ERIC HURST, and JOHN READ (*T.*, 1923, 123, 1657—1670).

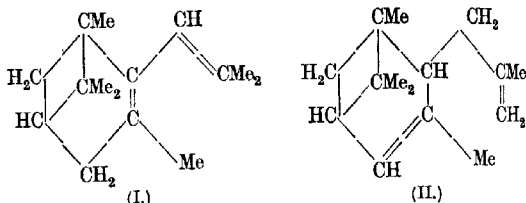
**The Conversion of Sabinol into Thujene.** GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON (*T.*, 1923, 123, 1713—1717).

**A New Method of Preparing Camphene.** H. PARISELLE (*Compt. rend.*, 1923, 176, 1901—1902).—By effecting the conversion of pinene into its hydrochloride in two stages, in order to minimise heating the material, the yield is increased to 75—85% of that theoretically possible. The use of sodium phenoxide for converting the hydrochloride into camphene is to be avoided, since the product cannot be freed from phenol or from unchanged hydrochloride. Using a mixture of crude *meta*- and *para*-cresols instead of phenol, an 88% conversion into camphene (b. p.  $51-53^{\circ}/17$  mm.) can be effected [cf. *J.S.C.I.*, 1923, Aug.].

E. E. T.

**Caryophyllene.** ERNST DEUSSEN (*Z. angew. Chem.*, 1923, 36, 348—349; cf. *Annalen*, 1912, 388, 155).—Oil of cloves contains both inactive  $\alpha$ -caryophyllene and the levorotatory  $\beta$ -isomeride, whereas the sesquiterpene in oil of hops, formerly known as humulene, has been identified as  $\alpha$ -caryophyllene. The latter gives a well-defined  $\alpha$ -nitrosochloride (m. p.  $177^{\circ}$ ) and  $\alpha$ -nitrosite

(m. p.  $161^{\circ}$ ), whilst the  $\beta$ -isomeride gives a blue, crystalline  $\beta$ -nitrosite (m. p.  $115^{\circ}$ ) possessing a very high specific rotation,  $[\alpha]_D^{25} +1666^{\circ}$  (in ligroin). The blue  $\alpha$ -caryophyllene nitrosite is optically inactive and melts at  $116^{\circ}$ .  $\beta$ -Caryophyllene is readily converted, by the action of nitrous acid, into a  $\gamma$ -isomeride, which forms a dihydrochloride identical with that of the  $\beta$ -isomeride. Neither the purified caryophyllene from oil of cloves nor  $\gamma$ -caryophyllene gives additive compounds with picric acid or *o*-nitrophenol, but the former yields well-defined additive products with mercurous sulphate and, in particular, with mercuric acetate below  $0^{\circ}$ . The products with the latter are converted into halides by means of potassium halides, and these compounds have the formula  $\text{OH}\cdot\text{Hg}\cdot\text{C}_{15}\text{H}_{24}\text{X}$ . They do not give the ionic reactions of mercury until treated with dilute hydrochloric or sulphuric acid. Treatment of the mercury additive compounds with potassium cyanide gives the corresponding cyanide, which is readily soluble in ether and is precipitated by light petroleum. The behaviour of caryophyllene towards sulphur, whereby a mixture of hydrocarbons,  $\text{C}_{15}\text{H}_{18}$ ,  $\text{C}_{14}\text{H}_{16}$  (?),  $\text{C}_{10}\text{H}_{14}$ , is produced, argues against its molecule containing a naphthalene skeleton. Reasons are given for regarding  $\beta$ -caryophyllene as being of the terpinolene type (I) and the  $\gamma$ -isomeride of the limonene type (II) (cf. Semmler, A., 1912, i, 120).



$\alpha$ -Caryophyllene must also contain two adjacent tertiary carbon atoms.  
W. T. K. B.

**A Sesquiterpene Alcohol from Elemi Oil.** H. JANSCH and P. FANTL (*Ber.*, 1923, 56, [B], 1363—1370).—The constituents of higher boiling point of elemi oil contain a bicyclic, singly unsaturated, tertiary sesquiterpene alcohol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , which is designated  $\alpha$ -elemol. The substance, elemol (now termed  $\beta$ -elemol) isolated by Semmler and Futung Liao (A., 1916, i, 492; cf. Semmler, A., 1908, i, 557) is not present as such in elemi oil, but is a secondary product derived from  $\alpha$ -elemol.

The elemi oil is submitted to fractional distillation under diminished pressure and the portion, b. p.  $140$ — $150^{\circ}/10$  mm., is thoroughly drained after it has solidified. It is purified by being repeatedly alternately spread on porous clay and distilled, whereby ultimately  $\alpha$ -elemol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , slender, almost odourless needles, m. p.  $46^{\circ}$ , b. p.  $142$ — $143^{\circ}/10$  mm.,  $n_D^{20} -2.73^{\circ}$  (50 mm. tube),  $d_4^{25} 0.94112$ ,  $n_D^{25} 1.49788$ , is obtained. It is converted by benzoyl chloride in the presence of pyridine into  $\beta$ -elemyl benzoate, b. p.

210—215°/10 mm.,  $n_D^{20}$  1.5408,  $d_4^{20}$  1.0346, which is hydrolysed by alcoholic alkali to  $\beta$ -elemol, b. p. 143—144°/10 mm.,  $d_4^{20}$  0.9419,  $n_D^{20}$  1.5070; these compounds are identical with those described by Semmler and Futung Liao (*loc. cit.*). The tertiary nature of the hydroxy-group of  $\alpha$ -elemol is established by its conversion by zinc dust at about 200° into *elemene*,  $C_{15}H_{26}$ , a colourless liquid, b. p. 115—119°/10 mm.,  $d_4^{20}$  0.8830,  $n_D^{20}$  1.4950.  $\alpha$ -Elemol is readily oxidised by permanganate or chromic acid and glacial acetic acid to ill-defined, acidic products; it is violently oxidised by nitric acid to (?) dinitrodihydrocuminic acid,  $C_{10}H_{12}O_6N_2$ , decomp. above 155° after darkening at about 140°. The presence of one double bond in  $\alpha$ -elemol is established by its hydrogenation in dry ethereal solution in the presence of spongy platinum to *dihydro- $\alpha$ -elemol*,  $C_{15}H_{28}O$ , m. p. 46°, b. p. 150—151°/11 mm. The action of bromine on  $\alpha$ -elemol in the presence of chloroform does not lead to the isolation of a homogeneous product.

H. W.

**Russian Essential Oils. I.** GEORGI VASILIEVITSCH PRIGULSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 60—71).—The investigation of the following oils is described: oil from *Pinus silvestris* (needles), *Abies sibirica* (needles and twigs), *Juniperus communis* (needles and twigs), *Mentha piperita*, and turpentine.

Two samples of pine needle oil were examined, both derived from the Viatka region (N.E. Russia). The first had  $d_4^{20}$  0.9155,  $[\alpha]_D^{20}$  -2.08°,  $[\alpha]_D^{25}$  -2.68°,  $[\alpha]_D^{30}$  -3.40°,  $[\alpha]_D^{35}$  -3.96°,  $[\alpha]_D^{40}$ /[ $\alpha]_D^{20}$ ] 1.90; acid number 7.48, saponification value 46.57 (calculated as bornyl acetate); after repeated fractionation the lowest fractions are dextrorotatory and possess a low rotatory dispersion; this may be due to the presence of  $\beta$ -pinene in addition to  $\alpha$ -pinene which was identified. Camphene could not be definitely identified, but was isolated (as isobornyl acetate) from the second sample examined; this had  $d_4^{20}$  0.9224,  $[\alpha]_D^{20}$  +3.84°,  $[\alpha]_D^{25}$  +4.94°,  $[\alpha]_D^{30}$  +6.54°,  $[\alpha]_D^{35}$ /[ $\alpha]_D^{20}$ ] 2.10, acid number 6.31, saponification value 44.91. The results obtained on fractionating the oil were similar to those above, the low fractions being dextrorotatory, but with a much higher rotation than those from the first sample; the higher fractions show levorotation.  $\alpha$ -Pinene is present, the presence of  $\beta$ -pinene could not be definitely established, but is probable owing to the anomalously low rotatory dispersion of some of the fractions. Both oils show a high ester content.

Two samples of Siberian fir-needle oil from *A. sibirica* were examined, one from the Viatka, the other from the Archangel district; they had almost identical physical properties, agreeing with those in the literature. Fractionation of these oils shows that with rise in boiling point the rotation and rotatory dispersion diminish. A sample of juniper oil (from *J. communis*, origin unknown) had  $d_4^{20}$  0.9258, acid number 10.71, saponification value 55.33 and was very feebly levorotatory. On fractionation it gave dextrorotatory low fractions, the higher fractions being levogyrate. The anomalous rotatory dispersion of the lowest (pinene) fraction points to the presence of nopinene.

Two samples of peppermint oil, one from the Pottava and the other from the Kursk district (Southern Russia) had almost identical properties; the first showed  $d_4^{20}$  0.9113,  $[\alpha]_D -21.96^\circ$ ,  $[\alpha]_D -27.66^\circ$ ,  $[\alpha]_D -35.14^\circ$ ,  $[\alpha]_D -41.84^\circ$ ,  $[\alpha]_D 1.91$ ; the free menthol content of the samples was high, being  $[\alpha]_D$  43.58 and 45.30, respectively.

Two samples of pine turpentine from the Viatka district were examined; the first, "red" turpentine, was purified by steam distillation (1) and had the following properties, those of the second, "colourless" sample (2), being shown for comparison:

|                        |                            |                            |                             |                            |                              |
|------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|------------------------------|
| (1) $d_4^{20}$ 0.8978, | $[\alpha]_D +7.20^\circ$ , | $[\alpha]_D +9.36^\circ$ , | $[\alpha]_D +12.40^\circ$ , | $[\alpha]_D 15.24^\circ$ , | $[\alpha]_D/[\alpha]_D$ 2.12 |
| (2) $d_4^{20}$ 0.8827, | $+5.16^\circ$ ,            | $6.66^\circ$ ,             | $8.80^\circ$ ,              | $10.66^\circ$ ,            | 2.07                         |

The acid numbers were 2.48 and 2.15, respectively. The results of fractional distillation and the rotations of the fractions are also given.

G. A. R. K.

**Russian Essential Oils. II.** G. V. PIGULEVSKI and (MILLER) V. S. NIKITINA (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 72-80).—Specimens of the following oils were examined: caraway, pennyroyal, laurel, thuja, spruce, and *Pinus densiflora*.

Of the three specimens of caraway oil from Kharkov district, two were obtained from the seeds and had the usual properties, the carvone content being from 47 to 56%; the third specimen was obtained from the crushed pulp and showed a higher density (0.9451), somewhat lower rotation ( $[\alpha]_D +65.34^\circ$ ), and a very high carvone content (79%).

The oil of pennyroyal which came from the Caucasus had the usual properties, the pulegone content being 75%.

The oil of the Caucasian spruce (*Picea orientalis*) obtained from the dry needles has the following properties:  $d_4^{20}$  0.9325,  $[\alpha]_D -28.39^\circ$ ,  $[\alpha]_D -36.38^\circ$ ,  $[\alpha]_D -47.42^\circ$ ,  $[\alpha]_D -58.10^\circ$ ,  $[\alpha]_D/[\alpha]_D$  2.05; the acid number is 2.17, the saponification value 97.95 (=26.42% bornyl acetate). Fractionation shows a comparatively small percentage of low-boiling hydrocarbons ( $\alpha$ - and  $\beta$ -pinene and camphene) compared with the oil of *P. vulgaris*; the ester content, on the other hand, is higher.

† The oil of the Caucasian fir (*Abies nordmanniana*) obtained from the dry needles had  $d_4^{20}$  0.9410,  $[\alpha]_D -29.66^\circ$ ,  $[\alpha]_D -38.12^\circ$ ,  $[\alpha]_D -49.68^\circ$ ,  $[\alpha]_D -60.82^\circ$ ,  $[\alpha]_D/[\alpha]_D$  2.05; acid number 3.06, saponification value 107.03 (=28.6% bornyl acetate), the values being similar to those for Siberian fir oil (cf. preceding abstract).

The specimens of Caucasian thuja oils were obtained from *Thuja gigantea* (i), *T. dolabrata* (ii), and *T. compacta* (iii). Their properties were:

|       | $[\alpha]_D$ | $[\alpha]_D$ | $[\alpha]_D$ | $[\alpha]_D$ | $[\alpha]_D/[\alpha]_D$ | Density.          | Solubility<br>in 80%<br>alcohol. |
|-------|--------------|--------------|--------------|--------------|-------------------------|-------------------|----------------------------------|
| (i)   | -1.68°       | -3.14°       | -5.90°       | -9.22°       | 5.49                    | $d_4^{20}$ 0.9260 | 1:0.6                            |
| (ii)  | +12.98°      | +16.00°      | +19.64°      | +22.48°      | 1.73                    | $d_4^{20}$ 0.9204 | 1:0.6                            |
| (iii) | +2.24°       | +2.60°       | +2.80°       | +2.40°       | 1.07                    | $d_4^{20}$ 0.9568 | 1:0.6                            |

The acid numbers and saponification values were (i) 5.96 and 32.03, (ii) 3.17 and 25.67, (iii) 6.85 and 43.40.

The oil of the Caucasian pine (*Pinus densiflora*) was prepared from the dry needles (i) in a yield of 0.37% and cones (ii) in a yield of 0.22%. The properties of two samples were:

|      | $[\alpha]_D$ | $[\alpha]_D$ | $[\alpha]_D$ | $[\alpha]_D$ | $[\alpha]_D/[\alpha]_C$ | Density.            | Solubility<br>in 80%<br>alcohol. |
|------|--------------|--------------|--------------|--------------|-------------------------|---------------------|----------------------------------|
| (i)  | -29.98°      | -38.34°      | -49.75°      | -60.81°      | 2.03                    | $d_{17.5}^4$ 0.9124 | 1:7                              |
| (ii) | -23.72°      | -30.28°      | -39.28°      | -47.44°      | 2.00                    | $d_{16.1}^4$ 0.9602 |                                  |

The acid numbers and saponification values were (i) 1.50 and 91.21, (ii) 7.60 and 103.04; sample (ii) has thus the higher density and percentage of esters. The oil is characterised by the high ester content.

The oil from laurel leaves (*Laurus nobilis*) of Caucasian origin is shown to be similar to the Crimean oil, and does not differ greatly from other European oils.

G. A. R. K.

**Russian Essential Oils. III.** G. V. PIGULEVSKI and U. A. PLOTNITZKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 81—86).—The preparation of the following oils from plants grown in the Crimea is described:

*Hyssopus officinalis*, *Salvia officinalis*, *Cupressus sempervirens*, and *Juniperus excelsa* M.R. (*J. sabina* var. *taurica* Pall.). The preparation of turpentine from the resin of *Pinus silvestris* and *P. taurica* was also carried out and the yield from the latter is shown to be comparable with that of French turpentine from *P. maritima*. Samples of this turpentine have  $[\alpha] -32.11^\circ$  and  $-32.53^\circ$ ,  $[\alpha]_D/[\alpha]_C$  1.95 and 2.01; whilst the turpentine from *P. silvestris* is also levorotatory ( $[\alpha]_D -17.48^\circ$  and  $-13.94^\circ$ ,  $[\alpha]_D/[\alpha]_C$  1.74 and 1.59).

G. A. R. K.

**Russian Essential Oils. IV.** G. V. PIGULEVSKI and (MME) S. S. FICHTENHOLZ (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 87—95).—The properties of hyssop, savin, and cypress oils prepared by Pigulevski and Plotnitzki (preceding abstract) are described.

Several samples of hyssop oil were examined and the properties of oils from blue-, red-, and white-flowered varieties are compared. The effect of keeping the raw material before subjecting it to distillation is discussed. The properties of the oils do not differ greatly from those of French oils. The greater part of the oil distils between  $203^\circ$  and  $217^\circ$  and this fraction shows the highest rotation.

A sample of savin oil (from the needles and young twigs of *Juniperus sabina* var. *taurica*) had  $d_{16.5}^{20}$  0.8896,  $[\alpha]_D +23.16^\circ$ ,  $[\alpha]_D +29.20^\circ$ ,  $[\alpha]_D +37.24^\circ$ ,  $[\alpha]_D +44.52^\circ$ ,  $[\alpha]_D/[\alpha]_C$  1.92, acid number 2.67, ester value 14.32 before and 44.55 after acetylation; the properties of a second sample were very similar.

The results of fractionation of the oil, and the effect due to the age of the needles from which it is derived, are also discussed.

The oil obtained from cypress twigs and needles shows properties

agreeing with those of French oils but the ester value is higher (26.11 before and 82.21 after acetylation); the results of fractionation are described.

G. A. R. K.

**Physico-chemical Studies on Caoutchouc. I. The Viscosity-Concentration Formula for Caoutchouc Solutions.**

KENICHI SHIMADA (*J. Chem. Ind. Japan*, 1923, 26, 705—708).—Viscosities of benzene solutions (0.03—0.47%) of caoutchouc at 15° have been determined by means of Ostwald's viscosimeter. The viscosities conform to Arrhenius's viscosity formula,  $\log \eta/\eta_0 = \frac{C}{C_0}$ , where  $\eta$  is the viscosity of the solution,  $\eta_0$  that of the solvent, and  $C$  the concentration of the system. The presence of resin in raw caoutchouc is without effect on the relation between viscosity and concentration.

K. K.

**Higher Terpene Compounds. X. Isomerism Phenomena among the Pine Resinic Acids of the Abietic Acid Group.**

L. RUZICKA and H. SCHINZ (*Helv. Chim. Acta*, 1923, 6, 662—673).—Modern American colophony is prepared from the crude resin at a comparatively low temperature, not exceeding 150°, and the abietic acid prepared from it is difficult to crystallise and is *d*-rotatory. By distillation at 0.3 mm. and crystallisation it gives the *l*-rotatory abietic acid previously described, m. p. 158° (Ruzicka and Meyer, A., 1922, i, 547). It is a general rule that the abietic acid of low temperature colophony undergoes inversion at about 250°, and a second inversion, becoming again *d*-rotatory, at 300°. The first inversion is also brought about by boiling acetic acid. French colophony has sometimes a small positive, sometimes a negative rotation. The former may be accounted for by the isomerisation of *l*-pimaric acid, which is present in French white resin (galipot), during the preparation of the colophony. When distilled in a high vacuum it behaves similarly to American colophony, but unlike the latter does not decompose into hydrocarbon when distilled at 12 mm. The abietic acid obtained has, after recrystallisation, m. p. 159—161°,  $[\alpha]_D -59^\circ$  to  $63^\circ$ , and appears identical with that from American colophony.

From a natural Swiss pine resin, care being taken not to heat above 60°, an abietic acid was obtained forming rectangular, colourless crystals, m. p. 142—144°,  $[\alpha]_D -138^\circ$  in alcohol. By catalytic reduction this gave a tetrahydro-derivative, m. p. 168—170°,  $[\alpha]_D +19^\circ$ . Crystallographically this acid appears to be related to the so-called *l*-pimaric acid. After boiling with acetic acid and recrystallising it had m. p. 162—164°,  $[\alpha]_D -92^\circ$ , and was closely similar crystallographically to the high temperature abietic acid from American colophony, forming hemimorphic monoclinic crystals. The angles of the crystals are very similar to those of a number of different abietic acids of m. p. from 155° to 180° and  $[\alpha]_D$  from  $+3^\circ$  to  $-180^\circ$ . It seems probable that the abietic acids may form a wide range of mixed crystals.

E. H. R.

**Higher Terpene Compounds. XI. *d*-Pimaric Acid and the Classification of the Pine Resin Acids.** L. RUZICKA and FR. BALAS (*Helv. Chim. Acta*, 1923, 6, 677—691).—To throw

further light on the chemical relationship between the *d*-pimaric acid of French white resin (galipot), and the abietic acid of American colophony, attempts have been made to elucidate the constitution of the former. According to Tschugaev and Teearu (A., 1913, i, 726), by catalytic hydrogenation it takes up two atoms of hydrogen, and it is probably a tetracyclic compound containing a single unsaturated bond. The molecular refractions of methyl and ethyl *d*-pimarate, however, agree with the values calculated on the assumption that the molecule contains two double bonds. Methyl *d*-pimarate has  $d_D^{20}$  1.030,  $n_D^{20}$  1.5208, and ethyl *d*-pimarate  $d_D^{20}$  1.013,  $n_D^{20}$  1.5151. In each case the determinations were made on the supercooled liquid. It was confirmed that only a dihydro-derivative of *d*-pimaric acid could be obtained by hydrogenation, but an ozonide was obtained, m. p. 90° (decomp.), having the formula  $C_{20}H_{28}O_2O_3$  or  $C_{20}H_{30}O_2O_3$ , which might be a triozonide of the unchanged *d*-pimaric acid or of a dehydro-acid,  $C_{20}H_{28}O_2$ . The dihydro-*d*-pimaric acid obtained by hydrogenation had m. p. 239–240°,  $[\alpha]_D^{20} +14.5^\circ$  in 0.5% alcoholic solution; a less pure fraction had m. p. 225–228° and it appears that a mixture of dihydro-acids is formed. The acid, m. p. 239–240°, crystallises in rhombic plates,  $[a : b : c = 0.681 : 1 : 1.892]$ , and is morphologically very close to *d*-pimaric acid,  $[a : b : c = 0.7056 : 1 : 1.8936]$ . By dehydrogenation of *d*-pimaric acid with sulphur at 250°, a hydrocarbon was obtained,  $C_{18}H_{14}$ , which appears to be a *dimethylphenanthrene*, m. p. 86°. It forms a *picrate*, yellow needles, m. p. 131–132°, and *styphnate*, m. p. 159°. When oxidised with chromic acid, it gives a *quinone*,  $C_{16}H_{12}O_2$ , red needles, m. p. 166°, which condenses with *o*-phenylenediamine to form a *quinoxaline*, needles, m. p. 194°. The pine resinic acids,  $C_{20}H_{30}O_2$ , can now be definitely divided into two groups, the abietic acid group, the members of which, when dehydrogenated, give retene, and the new group of which *d*-pimaric acid is the first representative.

A number of improvements in the methods of preparation of *d*- and *l*-pimaric acids from galipot are described. E. H. R.

**Higher Terpene Compounds. XII. Fichtelite and the Stereochemistry of Hydrogenated Phenanthrene Derivatives.** L. RUZICKA, FR. BALAS, and H. SCHINZ (*Helv. Chim. Acta*, 1923, 6, 692–697).—Although fichtelite has generally been recognised as a hydrogenated retene the relationship has never been proved. Retene has now been obtained from fichtelite by heating it with sulphur at 180–250° during twenty hours. It is pointed out that the formula of fichtelite is still uncertain, the choice lying between  $C_{18}H_{32}$  and  $C_{18}H_{34}$ . The molecular refraction does not distinguish between the two.

With regard to the stereochemistry of hydrogenated phenanthrene derivatives, it is pointed out that when the two carbon atoms common to two rings are united by a double bond the two rings must lie in a plane, but when the bond between these two carbon atoms is single, the two rings are in different planes. In the case of a three-ring system such as phenanthrene, when the system is fully hydro-

generated the three rings will all lie in different planes and *cis-trans* isomerism becomes possible. In the case of dodecahydrophenanthrene derivatives containing different substituents in the two outer rings, another kind of isomerism becomes possible due to the fact that the one double bond may be situated between the first and second or the second and third rings. The isomerism, sometimes of a labile nature, of retene and abietic acid derivatives may be due to these factors. E. H. R.

**The Synthesis of Æsculin.** E. GLASER and M. KRAUS (*Biochem. Z.*, 1923, **138**, 182—191).—When æsculetin is dissolved in cold potassium or sodium hydroxide solution and treated with an acetone solution of tetra-acetylglucose, according to Mauthner's method (A., 1910, i, 677; 1911, i, 647; 1912, i, 570; 1914, i, 195), æsculetintetra-acetylglucoside,  $C_6H_5O_4 \cdot C_6H_7O_5 \cdot Ac_4$ , is obtained, in 50% yield, as white, compact, prismatic crystals, m. p. 181—182°,  $[\alpha]_D^{20} -21^\circ$  in methyl alcohol ( $c=466$ ). Æsculin (æsculetinglucoside),  $C_6H_5O_4 \cdot C_6H_{11}O_5 \cdot 2H_2O$ , was obtained in 60% yield from the tetra-acetylglucoside by hydrolysis with baryta or, preferably, alcoholic ammonia, as white needles, m. p. 205°,  $[\alpha]_D^{20} -146^\circ$  in methyl alcohol ( $c=0.767$ ). It loses  $1\frac{1}{2}$  mols.  $H_2O$  at 100° and the rest of its water of crystallisation at its melting point. Synthetic æsculin gives all the reactions of the natural product but does not show fluorescence. It is suggested that the fluorescence of the natural glucoside is due to the presence of traces of impurities or decomposition products. J. P.

**The Synthesis of Protocatechualdehyde Glucoside.** E. GLASER and S. UEBERALL (*Biochem. Z.*, 1923, **138**, 192—197).—Protocatechualdehydetetra-acetylglucoside,  $C_7H_5O_3 \cdot C_6H_7O_5 \cdot Ac_4$ , obtained by Mauthner's method (cf. preceding abstract), forms white needles, m. p. 179—180°,  $[\alpha]_D^{20} -49.5^\circ$  in ethyl alcohol ( $c=677$ ). Hydrolysis with baryta (used in preference to alcoholic ammonia) gave protocatechualdehydegucoside,  $C_7H_5O_3 \cdot C_6H_{11}O_5$ , in 50% yield. It forms white, hygroscopic needles, m. p. 73—74°,  $[\alpha]_D^{20} -36.2^\circ$  in water ( $c=2.405$ ), and is hydrolysed by emulsin. Evidence is adduced in favour of the view that the glucose residue is attached to the *p*-hydroxyl group of protocatechualdehyde. J. P.

**Constituents of *Monotropa hypopitys*, L.; Preparation of a New Glucoside, Monotropein.** MARC BRIDEL (*Compt. rend.*, 1923, **176**, 1742—1744).—The prolonged action of emulsin on an alcoholic extract of *Monotropa hypopitys* resulted in an inversion of the rotation and a large increase in the percentage of reducing sugars. At the same time a blue colouring matter was developed. This behaviour pointed to the presence of a glucoside, monotropein, which was eventually isolated in the form of colourless and odourless prisms with a pronounced acid taste. The glucoside decomposes hydrogen carbonates with evolution of carbon dioxide and has  $[\alpha]_D^{20} +130.44^\circ$ . It is hydrolysed by 3% sulphuric acid with formation of a black precipitate similar to that given by aucubin, but the two glucosides are by no means identical. Emulsin hydrolyses

monotropein with formation of the above-mentioned blue substance. The darkening of the plant on drying is to be attributed to the presence of the glucoside.

G. F. M.

**Preparation of Verbenalin.** J. D. RIEDEL, *AKT. GES.* (D.R.-P. 358873; from *Chem. Zentr.*, 1923, ii, 337).—Extracts from plant material are purified by precipitation with solutions of salts of the alkaline earths or of heavy metals. The glucoside is then precipitated from the filtrate with ammonia and lead acetate. The aqueous solution obtained after decomposition of the precipitate is concentrated and the glucoside extracted by an organic solvent such as ethyl acetate. *Verbenalin* forms colourless prisms, m. p. 179–180° (uncorr.).

G. W. R.

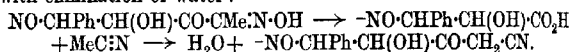
**Theory of Vegetable Tanning. I. Dehydration of Lyophilic Sols and Gels by Tannins and its Bearing on the Theory of Vegetable Tanning.** H. G. BUNGENBERG DE JONG (*Rec. trav. chim.*, 1923, 42, 437–472).—The investigations described deal with the following points: (1) whether the disperse phase in an aqueous solution of tannic acid has a capillary electric charge; (2) the mechanism of the precipitation of lyophilic bio-colloids with tannic acid; (3) the dehydration of an agar sol by tannic acid; (4) the rehydration of colloids dehydrated with tannic acids; (5) the character of some commercial tannic extracts; (6) the dehydration of gels with special reference to the theory of vegetable tanning.

The following results were obtained: (1) No capillary electric charge could be found with carefully purified tannic acid either by means of viscosimetry or cataphoresis. (2) In general, impure lyophilic bio-colloids are precipitated with tannin whether they are negatively charged (colloid carbohydrates) or positively charged (proteins). Specially purified lyophilic colloids, however, are not usually precipitated with tannin. (3) On addition of tannin to sols of specially purified agar or gelatin, the latter change into hydrophobic systems of which the capillary electric charge remains unaltered; considerable dehydration was indicated by viscosimetric measurements. (4) With impure lyophilic colloids the presence of electrolytic impurities frequently causes the capillary electric charge to fall below the critical value so that directly after dehydration precipitation by the tannin begins. Similarly with specially purified proteins precipitation takes place in the neighbourhood of the isoelectric point since here also the charge is below the critical value. (5) The dehydrations are connected with the adsorption of the tannin by the lyophilic particles and it is suggested that polar molecules are in general adsorbed in an orientated state in accordance with the views of Langmuir and Harkins. Hence after the adsorption the surface of the particles consists of feebly lyophilic phenolic groups so that there is little further opportunity for hydration. (6) On heating or on the addition of organic liquids miscible with water, rehydration occurs to a greater or lesser extent, as was found in making viscosimetric measurements with an agar sol. The degree of rehydration varies

with the nature of the lyophilic sol. (7) Viscosimetric measurements with an agar sol showed that the addition of sodium hydroxide also causes rehydration, but in this case there are no individual differences with lyophilic bio-colloids as the rehydration is equally complete in all cases, due to the neutralisation of the adsorbed tannin whilst the sodium tannate so formed is not adsorbed. (8) Commercial tanning extracts have, like tannin, a dehydrating effect on lyophilic colloids. In some of these extracts charged lyophilic colloids are present as an impurity which are dehydrated by the excess of tannin after cooling the extract. The behaviour of the extracts on heating, cooling, adding alcohol or sodium hydroxide, etc., agrees with this point of view. (9) Tannin has, like alcohol, a dehydrating effect on gels of lyophilic bio-colloids as seen in the case of agar. (10) Vegetable tannin is in the first place a physical dehydration of the lyophilic gel elements as a result of the adsorption of tannin.

F. A. M.

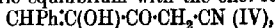
**Action of Nitrous Gases on Unsaturated Compounds.**  
**The Action of Nitrogen Trioxide on the Monoxime of Benzylidenediacetyl.** OTTO DIELS (*Annalen*, 1923, 432, 1—45).—The action of nitrogen trioxide on benzylidenediacetyl monoxime in dry ethereal solution leads to the formation of the bisnitroso-compound,  $\text{N}_2\text{O}_2[\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}]_2$ , m. p. 118—120° (decomp.), in the formation of which two  $-\text{O}\cdot\text{NO}$  groups in the initial product must become hydrolysed to hydroxyl groups, and the compound thus produced must then undergo a Beckmann interconversion of the "second type" (Werner and Pignet, A., 1905, i, 66; Diels and Stern, A., 1907, i, 480), with elimination of acetonitrile, which then condenses with the residual molecule with elimination of water:



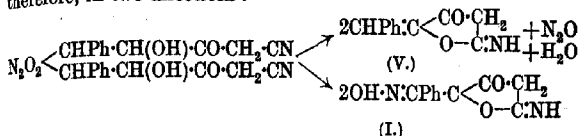
The bisnitroso-compound is insoluble in the usual solvents in the cold, but on warming with neutral solvents, whereby an unstable, green nitroso-compound is apparently first produced, with glacial acetic acid, or with moist or dry acetone, or by treatment with cold pyridine, it passes, with evolution of gas, into a bright yellow compound (see below). If boiling moist acetone is used, the oxime (I); pale yellow crystals, m. p. 158° (decomp.), is also formed; this may be hydrolysed to the ketone,  $\text{COPh}\cdot\text{CH} < \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{O}\cdot\text{C}\cdot\text{NH} \end{smallmatrix}$  (II),

transparent, rod-like crystals, m. p. 152—153° (decomp.), by means of concentrated hydrochloric acid.

$\beta\gamma$ -Diketo- $\delta$ -phenylvaleronitrile,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$  (III), intensely yellow, rod-like, monoclinic holohedral crystals, m. p. 138—139° (decomp.), is most conveniently prepared by the action of ice-cold pyridine on the bisnitroso-compound. The reactions of this substance, referred to hereunder as "the yellow compound," are interpreted on the assumption that the diketo-nitrile (III) exists in tautomeric equilibrium with the enol form,



and that the compound may also react as the imino-lactone (V). The decomposition of the bisnitroso-compound proceeds, therefore, in two directions :



the nature of the solvent determining which kind of decomposition will predominate.

Oxidation of the yellow compound in chloroform solution by means of ozone, and decomposition of the ozonides by means of boiling water, gives benzoic acid and dibenzylidene diperoxide, derived, through benzaldehyde, from the benzylidene part of the molecule (IV); the remainder of the molecule is completely destroyed.

The reduction of the yellow compound by means of zinc dust and hydrochloric acid in aqueous methyl-alcoholic solution gives *γ*-hydroxy-*β*-keto-*δ*-phenylvaleronitrile,  $\text{CH}_2\text{Ph-CH(OH)-CO-CH}_2\text{-CN}$  (VI), colourless, glistening needles, m. p. 104–105°, for which, however, the formula  $\text{CH}_2\text{Ph-C} \begin{array}{c} \text{C(OH)-CH}_2 \\ \text{O-C:NH} \end{array}$  (VII) is preferred,

the keto form of which,  $\text{CH}_2\text{Ph-CH} \begin{array}{c} \text{CO-CH}_2 \\ \text{O-C:NH} \end{array}$  (VIII), may also

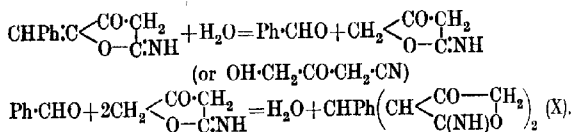
be capable of existence. This reduction product gives a *benzoate*, stout crystals, m. p. 54·5°, and dissolves unchanged in concentrated hydrochloric acid. It is decomposed by boiling with dilute aqueous alkali hydroxide, with evolution of ammonia; it reduces Fehling's solution or ammoniacal silver nitrate in the cold. In contrast to the yellow compound (see below), the reduction product does not form an additive compound with aniline or phenylhydrazine. When it is heated at 140°, carbon monoxide and toluene are evolved; the residue from this experiment, or the reduction product itself, gives phenylacetic acid, when oxidised by means of ozone. The reduction product spontaneously undergoes oxidation, accompanied by liquefaction, in contact with air, or rapidly in an atmosphere of oxygen; phenylacetic acid (the chief product), benzaldehyde, benzyl alcohol, acetic acid, and an indefinite nitrogenous residue are formed, the main reaction probably being:  $(\text{VII}) + \text{O}_2 + 2\text{H}_2\text{O} = \text{CO}_2 + \text{NH}_3 + \text{CH}_2\text{Ph-CO}_2\text{H} + \text{Me-CO}_2\text{H}$ .

When the yellow compound is boiled with benzene for three hours, an equivalent quantity of carbon monoxide is evolved, with formation of a *compound*,  $\text{C}_{23}\text{H}_{35}\text{O}_3\text{N}_2$ , white, matted crystals, m. p. 189° (decomp.), together with a viscous, reddish-orange gum. The action of hydrochloric acid and acetic acid at 150° on the compound  $\text{C}_{23}\text{H}_{35}\text{O}_3\text{N}_2$  gives a *compound*,  $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}$ , elongated prisms, m. p. 175°, which is gradually decomposed by boiling with concentrated potassium hydroxide solution, but without the evolution of ammonia.

The yellow compound forms additive compounds with methyl or ethyl alcohol, aniline, *o*-phenylenediamine, or phenylhydrazine. Since these products are colourless, it is suggested that addition occurs at the double bond of the individual (VIII). The compound,  $C_{14}H_{13}O_3N$ , from methyl alcohol, gradually dissociates, when kept in a vacuum. The compound,  $C_{17}H_{16}O_2N_2$ , m. p. 121–122° (decomp.), from aniline, and the compound,  $C_{17}H_{17}O_2N_3$ , m. p. 118–119°, from *o*-phenylenediamine, behave as salts, being decomposed in the presence of acids, with reproduction of the yellow compound. The compound, 
$$\begin{array}{c} \text{NHPh}\cdot\text{NH} \\ \text{CH}_2\text{Ph} \end{array} > \text{C} \begin{array}{l} \text{CO}\cdot\text{CH}_2 \\ \text{O}\cdot\text{C}\cdot\text{NH} \end{array} \text{ (IX), m. p.}$$

123–124°, from the yellow compound and phenylhydrazine in cold alcoholic solution, breaks down, in boiling toluene solution, with evolution of carbon monoxide, and formation of the phenylhydrazide of phenylacetic acid,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ .

At higher temperatures, strong amine bases are able to cause the elimination of benzaldehyde from the yellow compound. Thus benzaldehydephenylhydrazone is formed when the yellow compound and phenylhydrazine are boiled in alcoholic solution. When the yellow compound is boiled with aqueous alcoholic ammonia, free benzaldehyde is formed, together with a compound (X), m. p. 175°, which reduces cold ammoniacal silver nitrate or warm Fehling's solution, is insoluble in acids, but soluble in cold dilute alkali, and is decomposed, with elimination of ammonia, by means of warm, dilute alkali. It is evidently formed according to the scheme :



It gives a *diacetyl* derivative, m. p. 96°, and an *additive* compound, white, matted crystals, m. p. 207°, with one molecule of phenylcarbimide. The same compound is produced, together with benzyldene-ethylamine, by the action of aqueous ethylamine on the yellow compound.

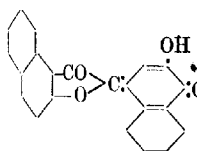
The yellow compound, reacting in the open-chain form (III), shows certain characteristic properties of nitriles. Thus, when fused with phosphorus pentachloride, it forms a colourless *additive* compound, which is soluble in ether, but is dissociated in the presence of water. A pale yellowish-red *additive* compound is likewise formed when the yellow compound and acetyl chloride are boiled with zinc chloride. Moreover, when the yellow compound and resorcinol are treated, in ethereal solution, in the presence of zinc chloride, with anhydrous hydrogen chloride, a colourless *additive* compound, white needles or prisms, m. p. 200–203°,  $+\text{CH}_3\cdot\text{CN}$ , colourless prisms, m. p. 150° (decomp.), is produced. The colourless reduction product (VI), or (VII) (VIII), does not undergo this reaction, presumably owing to the greater stability

of the imino-lactone phase (VII), or (VIII). The existence of the nitrile radicle in the yellow compound is also indicated by its behaviour when gently warmed with glacial acetic acid. Carbon monoxide is rapidly evolved, with formation of  $\beta\gamma$ -diketo- $\delta$ -phenylvaleric acid, white, matted needles, m. p.  $168^\circ$ , copper salt, hard, green prisms, methyl ester, b. p.  $105-110/0.6$  mm. During the production of this acid, a small quantity of phenylacetic acid is also formed; hence the generation of carbon monoxide. The diketo-acid gives benzaldehyde, and benzoic, oxalic, and acetic acids, when oxidised by means of ozone. It is decomposed by boiling with 95% formic acid into acetic and phenylpyruvic acids. A similar fission occurs when the acid is warmed with aqueous phenylhydrazine acetate, with production of phenylpyruvic acid and phenylhydrazone. The action of boiling anhydrous formic acid on the yellow compound is very similar; phenylpyruvic acid is produced, but partly decomposes, with elimination of carbon monoxide, and formation of phenylacetic acid.

A somewhat complicated reaction occurs when the yellow compound is boiled with a mixture of acetic acid and hydrochloric acid. Carbon monoxide, and some carbon dioxide, are eliminated, with production of phenylacetic acid and a dibasic acid,  $C_{20}H_{18}O_4N$ , glistening, matted leaflets, m. p.  $204^\circ$  (decomp.), acid pyridine salt, m. p.  $182^\circ$ , acid aniline salt, m. p.  $187-188^\circ$  (decomp.), in the formation of which three molecules of the yellow compound obviously participate. Its constitution has not, however, been elucidated.

The prolonged action of aqueous-ethereal hydrochloric acid on the yellow compound gives oxalic acid, whilst with boiling acetic anhydride, phenylacetic anhydride is produced. W. S. N.

**The Autoxidation of 1-Acetyl- $\beta$ -naphthol.** K. FRIES and H. EHLERS (*Ber.*, 1923, 56, [B], 1304-1308).—It has been shown

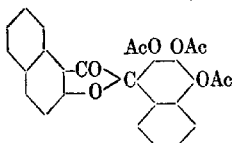


previously that 2-acetyl- $\alpha$ -naphthol undergoes a peculiar autoxidation in alkaline solution when the amount of alkali does not exceed a certain limit (cf. Fries and Leue, A., 1922, i, 462). Similar observations are now recorded with the isomeric 1-acetyl- $\beta$ -naphthol which yields acetic acid and a substance,  $C_{22}H_{12}O_4$ , to which, on account of its synthesis and reactions, the annexed constitution is assigned.

An improved method for the preparation of 1-acetyl- $\beta$ -naphthol is described in detail (cf. Fries and Frellstedt, A., 1921, i, 423).

When a solution of 1-acetyl- $\beta$ -naphthol in the requisite amount of aqueous sodium hydroxide solution is evaporated to dryness in an open dish, the compound,  $C_{22}H_{12}O_4$  (see above), is obtained as slender, brilliant red needles, m. p.  $303^\circ$  after darkening at  $260^\circ$ ; the carboxy-derivative crystallises in reddish-brown needles, m. p.  $243^\circ$ . The parent substance is decomposed by boiling aniline into 4:5-benzocoumaran-3-one and anilino- $\beta$ -naphthaquinone. It

is produced synthetically from 4:5-benzocumaran-3-one and 3-hydroxy-1:4-naphthaquinone-4-anil in the presence of boiling glacial acetic acid or, less advantageously, from 4:5-benzocumaran-3-one



and  $\beta$ -naphthaquinone in boiling alcoholic solution; the production of smaller amounts of blue and green substances is also observed (cf. this vol., i, 829). The compound,  $C_{22}H_{12}O_4$ , is converted by acetic anhydride containing a little concentrated sulphuric acid into the triacetate (annexed formula), colourless

needles, m. p.  $223^\circ$ , which loses acetic anhydride at  $150^\circ$  and passes into the yellow monoacetate.

4:5-Benzocumaran-3-one is conveniently prepared by the successive action of phosphorus pentachloride and aluminium chloride on the  $\beta$ -naphthyl ether of glycollic acid in the presence of benzene.

4-Bromo-2-acetyl- $\alpha$ -naphthol is unaffected by oxygen in the presence of an equivalent amount of aqueous sodium hydroxide solution or by lead peroxide in the presence of boiling glacial acetic acid. It is converted by nitric acid (*d* 1.5) and glacial acetic acid into 4-nitro-2-acetyl- $\alpha$ -naphthol, yellow needles, m. p.  $159^\circ$ . Under similar conditions, 4-bromo-2-ethyl- $\alpha$ -naphthol is transformed into 2-ethyl-1:4-naphthaquinone.

H. W.

**Thioflavanones, Thiochromanones, and Thiochromanols.** F. ARNDT [with W. FLEMMING, E. SCHOLZ, and V. LÖWENSOHN] (*Ber.*, 1923, 56, [B], 1269—1279).—The recent publications of Krollpfeiffer and Schäfer (this vol., i, 343) and of Zahn (this vol., i, 375) have caused the authors to publish an account of work which is not quite completed.

$\beta$ -*p*-Tolylthiol- $\beta$ -phenylpropionic acid,  $C_6H_4Me \cdot S \cdot CHPh \cdot CH_2 \cdot CO_2H$ , colourless needles, m. p.  $106^\circ$ , is prepared in 63% yield by the action of a mixture of saturated solutions of hydrogen bromide and hydrogen chloride in glacial acetic acid on cinnamic acid and *p*-thiocresol at  $100^\circ$ ; it is purified by means of its sparingly soluble sodium salt.  $\beta$ -Phenylthiol- $\beta$ -phenylpropionic acid, coarse, colourless needles, m. p.  $85$ — $86^\circ$ , is prepared in an analogous manner. Ring closure with the *p*-tolyl acid is effected by heating it on the water bath with phosphoryl chloride whereby 6-methylthioflavanone,  $C_6H_4Me \cdot \begin{smallmatrix} CO \cdot CH_2 \\ S - CHPh \end{smallmatrix}$ , colourless needles, m. p.  $96^\circ$ , is

obtained. The reaction can also be effected by the action of phosphoric oxide in the presence of boiling benzene, but, in this case, 6-methylthioflavone,  $C_6H_4Me \cdot \begin{smallmatrix} CO \cdot CH \\ S - CPh \end{smallmatrix}$ , m. p.  $149$ — $150^\circ$

(Ruhemann [A., 1913, i, 1374] gives m. p.  $153$ — $154^\circ$ ) is also produced by some unexplained process of oxidation. Thioflavanone crystallises in coarse, colourless needles, m. p.  $55$ — $56^\circ$ . 6-Methylthioflavanone condenses with benzaldehyde in the presence of hydrogen chloride to yield 3-benzylidene-6-methylthioflavanone, m. p.  $108$ — $109^\circ$ , identical with the product described previously

by von Auwers and Arndt (A., 1909, i, 668). 3-Benzylidenethioflavanone forms pale yellow crystals, m. p. 132—133°. The phenylhydrazone of 6-methylthioflavanone crystallises in long, colourless needles, m. p. 206°.

The conversion of the thioflavanones into thioflavanols has not yet been successfully accomplished. The conversion of the former into oximino-derivatives by amyl nitrite and hydrochloric acid or other agents does not take place to an appreciable extent under mild conditions, whereas under more drastic treatment oxidative elimination of benzoic acid occurs with formation of the thionaphthenquinone,  $C_6H_4Me \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} \diagup CO$ , pale red needles, m. p.

145—146°. The change gives another example of the tendency of the thionaphthen ring to contraction. On the other hand, the thioflavanones condense smoothly with nitrosobenzene or *p*-nitrosodimethylaniline, whereby 6-methylthioflavanol-*p*-dimethylaminoanil,  $C_6H_4Me \begin{smallmatrix} \diagup CO \cdot C \cdot N \cdot C_6H_4 \cdot NMe_2 \\ \diagdown S - CHPh \end{smallmatrix}$ , lustrous, brownish-red leaflets, m. p.

166—167°, thioflavanol-*p*-dimethylaminoanil, m. p. 124—125°, and two stereoisomeric forms of 6-methylthioflavanolanil, m. p. 91—92°, and yellow needles, m. p. 172—173°, are isolated. Fission of the *p*-dimethylaminoanils could not be effected, whereas the simpler anils regenerated the thioflavanones.

$\beta$ -*Tolythiolpropionic acid*,  $C_6H_4Me \cdot S \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , lustrous crystals, m. p. 70°, is obtained in almost quantitative yield by the action of *p*-tolylthiol dissolved in aqueous sodium hydroxide solution on  $\beta$ -chloropropionic acid (the preparation of the latter is described in detail).  $\beta$ -*Phenylthiolpropionic acid* crystallises in colourless leaflets, m. p. 58°. Ring closure of the substituted propionic acids is simply and almost quantitatively effected by concentrated

sulphuric acid, whereby 6-methylthiochromanone,  $C_6H_3Me \begin{smallmatrix} \diagup CO \cdot CH_2 \\ \diagdown S - CH_2 \end{smallmatrix}$ ,

colourless, crystalline leaflets, m. p. 41°, and thiochromanone, colourless leaflets, m. p. 28°, are obtained. The benzylidene derivative of 6-methylthiochromanone crystallises in coarse, yellow needles, m. p. 119.5°; it yields an additive product with hydrogen chloride, needles, m. p. 164°. The *p*-dimethylaminoanils of 6-methylthiochromanol, brownish-red crystals, m. p. 193°, and of thiochromanol, m. p. 142°, are described. Fission of the respective anils by boiling sulphuric acid (50—60%) leads to the production

of 6-methylthiochromanol,  $C_6H_3Me \begin{smallmatrix} \diagup CO \cdot C \cdot OH \\ \diagdown S - CH \end{smallmatrix}$ , coarse, pale yellow

crystals, m. p. 167—168°, and thiochromanol, transparent, pale yellow needles, m. p. 172°.

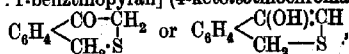
Attention is directed to the advantages of vacuum sublimation as a means of purifying organic compounds and various forms of apparatus are described in detail.

H. W.

#### 4-Hydroxyhomothionaphthen (4-Ketisoithiochroman).

RUDOLF LESSER and ALICE MEHRLÄNDER (Ber., 1923, 56, [B], 1642—1648).—The preparation of 4-hydroxyhomothionaphthen

[4-hydroxy-2:1-benzthiopyran] (4-ketoisothiochroman),



is described. The substance does not usually resemble  $\beta$ -hydroxy-thionaphthen in its behaviour, and reacts generally in the ketonic form.

S-Benzylthiolacetic acid,  $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 62–63°, after previous softening, is obtained by the condensation of benzyl mercaptan with chloroacetic acid or as its ethyl ester, b. p. 156–157°/11 mm., by use of ethyl chloroacetate. The barium salt,  $(\text{C}_6\text{H}_5\text{O}_2\text{S})_2\text{Ba}\cdot 2\text{H}_2\text{O}$ , lustrous, colourless platelets and the copper salt (+2H<sub>2</sub>O), pale bluish-green needles, are described. The acid is converted by thionyl chloride into benzylthiolacetyl chloride, a colourless, viscous liquid, b. p. 144–145°/11 mm. The latter substance is converted by aluminium chloride in the presence of nitrobenzene into 4-hydroxy-2:1-benzthiopyran, colourless leaflets, m. p. 60–61° after previous softening. The corresponding oxime,  $\text{C}_6\text{H}_5\text{ONS}$ , crystallises in pale yellow needles, m. p. 134–135°; it yields a sparingly soluble sodium salt. The benzoyl derivative of the oxime,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{NS}$ , forms colourless needles, m. p. 147–148°. 4-Hydroxy-2:1-benzthiopyran yields a p-nitrophenylhydrazide, red needles, m. p. 214°, and a ketazine,  $\text{C}_9\text{H}_8\text{S}\cdot\text{N}\cdot\text{N}\cdot\text{S}\cdot\text{H}_2\text{S}$ , slender, yellow needles, m. p. 229° after previous softening and darkening. Benzeneazo-4-hydroxy-2:1-benzthiopyran crystallises in pale red needles or rodlets, m. p. 139°. The action of p-nitrosodimethylaniline on 4-hydroxy-2:1-benzthiopyran in alcoholic solution in the presence of potassium hydroxide leads to the formation of p-dimethylaminophenylbishydroxy-2:1-benzthiopyranilamine,  $(\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CH}_2-\text{S} \\ \diagdown \text{C}(\text{OH}) \end{array})_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , m. p. 175–176°; the sodium and calcium salts are described. Bromo-4-hydroxy-2:1-benzthiopyran,  $\text{C}_6\text{H}_4\text{OBrS}$ , unstable, colourless, rhombohedral crystals, m. p. 89–90°, is obtained by the action of bromine on the naphthen dissolved in carbon disulphide.

O-Cyanobenzylthiolacetic acid, well-defined plates, m. p. 118–119°, is prepared by the action of  $\omega$ -thiolacetic acid on o-cyanobenzyl chloride in the presence of potassium hydroxide in aqueous-alcoholic solution; the corresponding amide,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , crystallises in colourless needles, m. p. 112–113°. O-Carboxybenzylthiolacetic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , colourless needles, m. p. 146–147°, is prepared by the action of aqueous sodium hydroxide solution (20%) on the corresponding nitrile; it is converted by boiling acetic anhydride and potassium acetate into 4-acetoxy-2:1-benzthiopyran, pale yellow crystals, m. p. 94–95°, which is converted by sodium hydroxide solution into 4-hydroxy-2:1-benzthiopyran.

Benzylthiolacetic acid dissolved in glacial acetic acid is oxidised by hydrogen peroxide (30%) to benzylsulphoneacetic acid,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , lustrous platelets, m. p. 137–138° after slight previous softening; the ammonium salt, silver salt, colourless needles and the dihydrated copper salt are described. The

chloride forms colourless crystals, m. p.  $95^\circ$  (indefinite); the *amide*, colourless leaflets, m. p.  $177-178^\circ$ , and the *anilide*, pale yellow, slender needles, m. p.  $171^\circ$ , were prepared. The action of aluminium chloride on the chloride in the presence of nitrobenzene causes total decomposition of the sulphone.

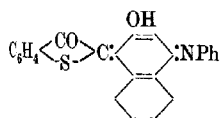
H. W.

**Dinaphthathiophen. I. The Action of Sulphuric Acid on Dinaphthathiophen.** K. DZIEWOŃSKI and M. PROKOPCZUK [*Wzrost Chemikow Polskich*, 1923, 56].—The sulphonation of dinaphthathiophen,  $C_{24}H_{12}S$ , is shown to be a reaction of extreme complexity. The nature of the products depends on the conditions of the process, and the products consist of sulphonic acids, oxidation, polymerisation, and condensation products of the various compounds formed, the following substances being isolated:  $C_{24}H_{12}O_6S_3$ ,  $C_{24}H_{12}O_6S_4$ ,  $C_{48}H_{20}O_6S_3$ ,  $C_{48}H_{18}O_5S_3$ ,  $C_{72}H_{24}O_{12}S_6$ ,  $C_{92}H_{40}O_{22}S_7$ . These are intensely coloured substances, the colours ranging from orange to black, and appear to be sulphonic acids, quinone-sulphonic acids, and sulphonosulphonic acids. They have the property of dyeing animal fibres, in some cases without the use of a mordant.

R. T.

**Indigoid Compounds from 3-Hydroxy-1:4-naphthaquinone-4-anil and Benzocumaranonones or Oxythionaphthen.** K. FRIES and H. EHLERS (*Ber.*, 1923, 56, [B], 1308-1319).—During the synthesis of the products obtained by the autoxidation of 2-acetyl- $\alpha$ -naphthol (Fries and Leuc, A., 1922, i, 462) and 1-acetyl- $\beta$ -naphthol (Fries and Ehlers, this vol., i, 825), the formation of minor amounts of blue and green compounds is invariably observed. The nature of these products has been elucidated and a series of analogous substances prepared.

The condensation of 3-hydroxythionaphthen with 2-hydroxy-1:4-naphthaquinone-4-anil in the presence of boiling glacial acetic acid leads to the formation of 3-hydroxy-4-keto-1-(oxythionaphthenylidene)dihydronaphthalene (Sachs and Ohlm, A., 1914, i, 552), red needles, m. p.  $224^\circ$ . With anilino- $\beta$ -naphthaquinone in the presence of alcohol and acetic anhydride, hydroxythionaphthen gives 2-thionaphthen-2'-hydroxynaphthalene-1'-indolignone-4'-anil [4-anilo-2-hydroxy-1-(oxythionaphthenylidene)dihydronaphthalene]

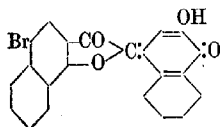


(annexed formula), dark red leaflets, m. p.  $242^\circ$ . 3-Hydroxythionaphthen and 2-anilino-1:4-naphthaquinone-4-anil yield 3-anilino-4-keto-1-(thionaphthenylidene)dihydronaphthalene, long, dark blue needles, m. p.  $234^\circ$ , which is converted by alcoholic potassium hydroxide solution into aniline and the corresponding 3-hydroxy-compound (described above); it can also be obtained by acting on the latter with aniline.

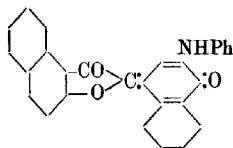
4-Anilino-1-keto-2-(thionaphthenylidene)dihydronaphthalene, greenish-blue or bronzy needles, m. p. about  $224^\circ$  (decomp.), is prepared from hydroxythionaphthen and 2-methoxy-1:4-naphthaquinone-4-anil in the presence of boiling glacial acetic acid; the corresponding *acetyl* derivative crystallises in pale red, lustrous

needles, m. p. 174°. The parent substance is converted by boiling aniline into 2-anilino-1:4-naphthaquinone-4-anil.

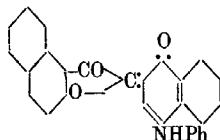
5-Bromo-6:7-benzocumaran-3-one and anilino- $\beta$ -naphthaquinone yield 3-hydroxy-4-keto-1-(5'-bromo- $\alpha\beta$ -benzcumaronylidene)dihydronaphthalene (annexed formula), lustrous red needles, m. p. 310° (decomp.) after incipient darkening at 285°. The corresponding 3-anilino-derivative crystallises in blue needles, m. p. 270° (decomp.).



4:5-Benzocumaranone and 3-anilino-naphthaquinoneanil react in boiling glacial acetic acid solution to yield 3-anilino-4-keto-1-( $\alpha\beta$ -benzcumaronylidene)dihydronaphthalene (annexed formula), blue needles, m. p. 280° (decomp.), and the green substance identical with that derived from benzocumaranone and 3-methoxy-1:4-naphthaquinone-4-anil.



4:5-Benzocumaran-2-one and 3-methoxy-1:4-naphthaquinone-4-anil (annexed formula), slender, dark green needles, m. p. about 280° (decomp.). 4-Anilino-1-keto-2-(5'-bromo- $\alpha\beta$ -benzcumaronylidene)dihydronaphthalene crystallises in slender, green needles, decomp. 232°.



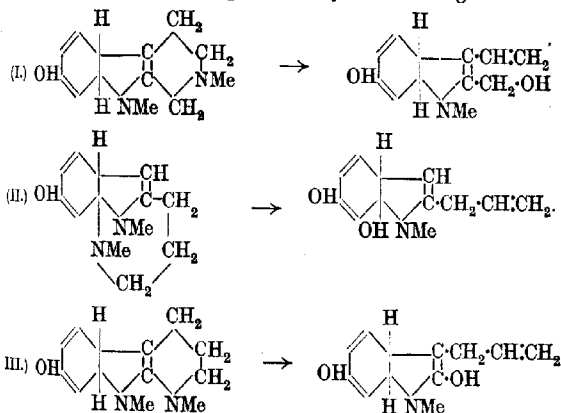
2:3-Dichloro-1:4-naphthaquinone condenses very readily with hydroxythionaphthen in alcoholic solution in the presence of a little alkali hydroxide; the primary product of the action is very readily converted by atmospheric oxygen into the substance,  $C_{28}H_{12}O_4S_2$  (annexed constitution), slender, almost black needles, m. p. above 360°. In a similar manner, 2:3-dichloro-1:4-naphthaquinone and benzocumaranone give the compound,  $C_{34}H_{16}O_6$ , slender, dark violet needles, m. p. above 360°. 2-Chloro-3-anilino-1:4-naphthaquinone gives the substance,  $C_{24}H_{12}O_2NS$ , dark red needles, m. p. above 360°, with hydroxythionaphthen and the compound,  $C_{28}H_{15}O_4N$ , slender, brilliant red needles, m. p. above 360°, with 4:5-benzocumaran-2-one.

**Method of Preparation of some Crystalline Alkaloidal Bismuthic Iodides.** MAURICE FRANÇOIS and LOUIS GASTON BLANC (*Bull. Soc. chim.*, 1923, [iv], 33, 640—654).—Details are given of the methods of preparation and analysis of numerous crystalline alkaloidal bismuthic iodides (cf. A., 1922, i, 851) of which a general description has already been given. An accurate estimation of the alkaloid, the iodine, and the bismuth in these

compounds was achieved by dissolving the substance in a solution of sodium tartrate containing an excess of sodium hydroxide. The iodine was thereby converted into alkali iodide and was estimated as silver iodide, the bismuth dissolved as sodium bismuthyl tartrate, and was estimated by precipitation from this solution as sulphide and weighing as oxide, whilst the alkaloid was extracted in the usual way with an immiscible organic solvent. In the preparation of the compounds the general method (*loc. cit.*) is followed with such modifications in detail as are necessitated by reason of their different solubilities. Full particulars are given of the preparation and composition of the bismuthic-iodides of caffeine, theobromine, nicotine, sparteine, arecoline, pilocarpine, atropine, quinine, morphine, codeine, and also of aniline  $(\text{BiI}_3)_4(\text{NH}_2\text{Ph.HI})_3$ , pyridine and quinoline, of analogous composition. In general, the bismuthic-iodides of the monoacidic alkaloids have the constitution  $(\text{BiI}_3)_4(\text{Alk.HI})_3$ , whilst the diacid alkaloids form compounds of the type  $(\text{BiI}_3)_2\text{Alk.HI}$ .

G. F. M.

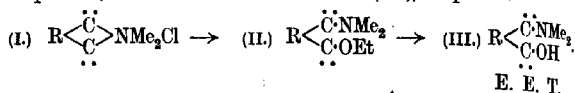
**The Constitution of Eserine.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, 176, 1896—1898).—The existence of an ethylenic linking in the pyrrole nucleus in etherseroline, and the ready formation, by the latter, of a methiodide, can only be explained by assuming the presence of a hydroindole structure (see below). The authors suggest provisionally three formulæ (I, II, and III) for eseroline, which agree better with its chemical behaviour than formulæ hitherto proposed for that substance. The degradation of eseroline to etherseroline, according to each formula, can be probably represented by the following schemes:



E. E. T.

**Eseretholemethine and its Alcoholate.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, 177, 127—129; *ibid.* this vol., i, 700).—Eseretholemethine, hitherto regarded as an

anhydro-base, actually behaves as if a free hydroxyl group were present. Thus hydriodic acid readily converts it into eserethole methiodide, and all of its derivatives contain one molecule of water which cannot in every case be considered simply as solvent of crystallisation. This view is supported by experiments on the conversion of the methine into the hydrochloride. If eserethole methochloride (I) is treated with alcoholic sodium ethoxide (1 mol.), in absence of water, an *ethoxide* (II) is formed (an oil,  $[\alpha]_D^{25} +114^\circ$ ), which is sparingly soluble in water, but, on heating in aqueous suspension, is converted into the methine (III), m. p.  $89^\circ$ :



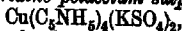
E. E. T.

**Some Bases of the Tropacocaine Type derived from  $\psi$ -Pelletierine.** GEORGES TANRET (*Compt. rend.*, 1923, 176, 1659—1662).—*n*-Methylgranatoline was obtained from  $\psi$ -pelletierine by reduction with sodium and absolute alcohol and was used as a starting point in the work described. *Benzoylmethylgranatoline*,  $\text{NMe}\cdot\text{C}_7\text{H}_{12}\cdot\text{CH}\cdot\text{OBz}$ , was obtained by the action of a benzene solution of benzoyl chloride at  $100^\circ$  (cf. Ciamician and Silber, A., 1894, i, 154) and is an almost colourless oil, b. p.  $230^\circ/24\text{ mm.}$ , yielding a *sulphate*, m. p.  $181^\circ$ , a *nitrate*, m. p.  $227^\circ$ , and a *methiodide*, m. p. above  $300^\circ$ . It has marked physiological properties, and experimental detail with respect to these is given. *Cinnamoylmethylgranatoline*, prepared by means of cinnamoyl chloride, readily forms crystals, m. p.  $62\text{--}63^\circ$ . *p*-Nitrobenzoylmethylgranatoline, from *p*-nitrobenzoyl chloride, forms pale yellow crystals, m. p.  $149\text{--}150^\circ$ , and yields a *hydrochloride*, white needles. *p*-Aminobenzoylmethylgranatoline was obtained from the nitro-derivative by reduction with iron and acetic acid, and forms white crystals, m. p.  $194\text{--}196^\circ$ . The general conclusion is drawn from a study of the local anæsthetic properties of these substances that the double piperidine ring of homotropacocaine yields derivatives of more marked action than those obtained from the piperidine-pyrrolidine nucleus of tropacocaine.

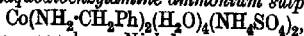
H. J. E.

**Complex Ammonium Salts.** G. SPACU and R. RÎPAN (*Bul. Soc. Ştiinţe Cluj*, 1922, 1, 473—496; from *Chem. Zentr.*, 1923, i, 674—676; cf. this vol., i, 96, and ii, 72).—The following complex salts are described: *copper tetrapyridine ammonium sulphate*,  $\text{Cu}(\text{C}_5\text{NH}_5)_4(\text{NH}_4\text{SO}_4)_2$ , a blue, crystalline powder prepared from anhydrous pyridine and copper ammonium sulphate; it is unstable in air, losing pyridine on exposure. *Copper hexammine ammonium sulphate*,  $\text{Cu}(\text{NH}_3)_6(\text{NH}_4\text{SO}_4)_2$ , is a blue, crystalline powder formed by the action of dry ammonia on the copper tetrapyridine ammonium sulphate; it is unstable in air. *Copper triaquotribenzylamine ammonium sulphate*,  $\text{Cu}(\text{NH}_2\cdot\text{CH}_2\text{Ph})_3(\text{H}_2\text{O})_3(\text{NH}_4\text{SO}_4)_2$ , a blue powder obtained by the action of benzylamine on copper ammonium sulphate, and *copper tribenzylamine ammonium sulphate*,  $\text{Cu}(\text{NH}_2\cdot\text{CH}_2\text{Ph})_3(\text{NH}_4\text{SO}_4)_2$ .

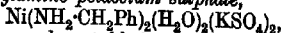
obtained similarly, using excess of benzylamine, are both stable in air. *Copper tetrapyridine potassium sulphate*,



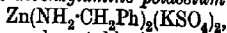
prepared by the action of anhydrous pyridine on copper potassium sulphate, is a blue, crystalline powder. *Copper tribenzylamine potassium sulphate*,  $\text{Cu}(\text{NH}_2\cdot\text{CH}_2\text{Ph})_3(\text{KSO}_4)_2$ , a blue, crystalline powder stable in air. *Cobalt tetra-aquodipyridine ammonium sulphate*,  $\text{Co}(\text{C}_6\text{NH}_5)_2(\text{H}_2\text{O})_4(\text{NH}_4\text{SO}_4)$ , a red, crystalline powder, unstable in air. *Cobalt diaquodibenzylamine ammonium sulphate*,



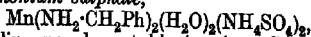
a red, crystalline powder. *Nickel aquopentapyridine potassium sulphate*,  $\text{Ni}(\text{C}_6\text{NH}_5)_5\cdot\text{H}_2\text{O}(\text{KSO}_4)_2$ , a green, crystalline powder. *Nickel diaquodibenzylamine potassium sulphate*,



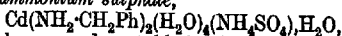
a brown, crystalline powder, stable in air. *Zinc tetra-aquodipyridine ammonium sulphate*,  $\text{Zn}(\text{C}_6\text{NH}_5)_2(\text{H}_2\text{O})_4(\text{NH}_4\text{SO}_4)_2$ , a white, crystalline powder, unstable in air. *Zinc tetra-aquodipyridine potassium sulphate*,  $\text{Zn}(\text{C}_6\text{NH}_5)_2(\text{H}_2\text{O})_4(\text{KSO}_4)_2$ , a colourless, crystalline powder unstable in air. *Zinc dibenzylamine potassium sulphate*,



a white, crystalline powder stable in air. *Manganese diaquodibenzylamine ammonium sulphate*,



a white, crystalline powder, stable in air. *Cadmium tetra-aquodibenzylamine ammonium sulphate*,



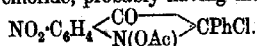
a white, amorphous powder, stable in air.

G. W. R.

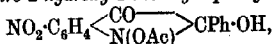
**Preparation of the Homologues of Isatin.** Preparation of 5-Bromo-7-methylisatin. (MILLÉ) MARCELLE RESSY and ANDRÉ P. ORTODOSU (*Bull. Soc. chim.*, 1923, [iv], 33, 637—640).—5-Bromo-7-methylisatin was synthesised from *o*-toluidine on the lines of Staudinger's synthesis of isatin from aniline. *o*-Toluidine was acetylated, and the acetyl-*o*-toluidide, m. p. 107°, gave on bromination *acetyl-p-bromo-o-toluidide*, m. p. 156·7°. The corresponding benzoyl compound melted at 115°. On hydrolysis of either of these compounds, *p-bromo-o-toluidine* was obtained, m. p. 57°. Condensation of the hydrochloride of this base with hydroxylamine hydrochloride and chloral hydrate gave a yellow product, the dibromodi-*o*-tolylamidine of the oxime of glyoxalic acid, which on hydrolysis was converted into *oximinoacetyl-bromo-o-toluidide*,  $\text{C}_6\text{H}_4\text{MeBr}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{NOH}$ , m. p. 181°. On warming this substance with sulphuric acid, a violet-blue solution was obtained from which water precipitated the desired 5-bromo-7-methylisatin, crystallising in long, red prisms, m. p. 240°. Its *phenylhydrazone* melts at 252°, and its *oxime* at 249°. Its colour is much deeper than that of either isatin or methylisatin owing to the accumulation of auxochromes and the increased molecular weight. G. F. M.

**Additive Compounds of the Isatogens.** P. RUGGLI, A. BOLLIGER, and W. LEONHARDT (*Helv. Chim. Acta*, 1923, 6, 594—604; cf. A., 1921, i, 811).—When 6-nitro-2-phenylisatogen is boiled

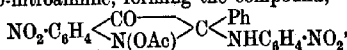
with acetyl chloride a yellow additive compound is formed with one mol. of acetyl chloride, probably having the formula



It crystallises in large, transparent prisms decomposing between  $145^\circ$  and  $160^\circ$  and is very sensitive to moisture, by which it is decomposed into its constituents. By ice, it is decomposed with formation of 6-nitro-2-hydroxy-1-acetoxy-2-phenylisatogen,

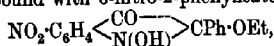


yellow needles, decomposing at  $125^\circ$ . This compound, which is more stable than the acetyl chloride compound, cannot be prepared directly from its constituents. The acetyl chloride compound reacts with *p*-nitroaniline, forming the compound,



m. p.  $214^\circ$ . In the same way, it reacts with methyl alcohol, forming a compound, m. p.  $164.5^\circ$ , and with ethyl alcohol, forming a compound, m. p.  $144.5-145^\circ$ ; in each case the chlorine atom attached to carbon is probably replaced by the alkyloxy group. Acetic anhydride also forms an additive compound when boiled with 6-nitro-2-phenylisatogen, but the reaction is incomplete. The compound forms yellow needles, m. p.  $195-198^\circ$ , when heated quickly; it probably has the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{<}\begin{array}{c}\text{CO} \\ \text{N(OAc)}\end{array}\text{>CPh-OAc.}$

Cold ethyl alcohol saturated with hydrochloric acid also forms an additive compound with 6-nitro-2-phenylisatogen,



yellow needles, decomposing at  $80-90^\circ$  into its constituents. This is isomeric with the compound formed with ethyl alcohol at higher temperatures (A., 1919, i, 221). The oxime of isonitrophenylisatogen previously described is now found to be identical with the *N*-oxime of the quinonoid form. E. H. R.

**3-Hydroxyquinoline Derivatives from the *N*-Benzylidene Compounds of *o*-Aminophenylacetic Acid.** A. KLEIGL and ADOLF SCHMALENBACH (*Ber.*, 1923, 56, [B], 1517-1520).—In a recent communication (A., 1922, i, 545), Neber has described the preparation of 3-hydroxy-2-*o*-nitrophenylquinoline by the action of heat on *o*-nitrobenzylidene-*o*-aminophenylacetic acid. The authors' failure to effect ring closure with a number of apparently similarly constituted substances has caused them to doubt the identity of the compound isolated by Neber. They find that the primary products of the action of heat on *o*-nitrobenzylidene-*o*-aminophenylacetic acid are *o*-nitrobenzaldehyde and oxindole, and that these substances react further with the ultimate formation of 3-*o*-nitrobenzylideneoxindole,  $\text{NH<}\begin{array}{c}\text{C}_6\text{H}_4 \\ \text{CO}\end{array}\text{>C:CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ .

*Pyruvilidene-o-hydrazinobenzoic acid*,  $\text{COMe}\cdot\text{CH:N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  long, yellow needles, decomp. about  $215^\circ$  after softening at  $200^\circ$ .

is prepared by the action of diazotised anthranilic acid on acetoacetic acid. It could not be caused to undergo ring closure by the action of heat. It is converted by phenylhydrazine into the *phenyl-osazone*,  $C_{18}H_{16}O_2N_4$ , yellow crystals, m. p. about  $215^\circ$  (decomp.) after softening at  $200^\circ$ , which is transformed by boiling glacial acetic acid into aniline and 1-o-carboxyphenyl-3-methyl-1:2:5-triazole,  $\begin{matrix} \text{CH=N} \\ \text{CMe:N} \end{matrix} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , a crystalline powder, m. p. about  $275^\circ$  (decomp.) after darkening at about  $240^\circ$ . H. W.

### 5:6:7:8-Tetrahydroquinolines and their Derivatives. II.

JULIUS VON BRAUN, WALTER GMELIN, and ADAM SCHULTHEISS (*Ber.*, 1923, 56, [B], 1338—1347).—It has been shown recently (this vol. i, 136) that whereas quinoline itself is readily hydrogenated to 1:2:3:4-tetrahydroquinoline, certain of its derivatives become similarly hydrogenated to a greater or less extent in the benzenoid portion of the molecule. The influence of substituents on the course of the hydrogenation has therefore been systematically investigated with the methylquinolines. The presence of a methyl group in positions 6, 7, or 8 causes the exclusive formation of 1:2:3:4-tetrahydro-compounds, and this is also probably true in the case of 5-methylquinoline, which, however, has not been examined. 3- and 4-Methylquinolines give a mixture of 33% of the 5:6:7:8- and 66% of the 1:2:3:4-tetrahydro-derivatives, whereas 2-methylquinoline yields 4% of the 5:6:7:8 and 96% of the 1:2:3:4-tetrahydro-compounds. The introduction of more methyl groups into the pyridine nucleus of the molecule causes the formation of a greater proportion of the 5:6:7:8-tetrahydro-substances.

The methylquinolines are hydrogenated under pressure in the presence of nickel, tetra- or deca-hydronaphthalene being used as solvents. The temperature is raised gradually until hydrogen commences to be absorbed, after which it is usually maintained approximately constant until reduction is complete. The secondary and tertiary bases in the products are separated from one another by exhaustive treatment with benzoyl chloride.

8-Methylquinoline yields exclusively 8-methyl-1:2:3:4-tetrahydroquinoline, b. p.  $126\text{--}129^\circ/12$  mm. (benzoyl derivative, m. p.  $108^\circ$ ; nitroso-compound, m. p.  $51^\circ$ ). 7-Methylquinoline gives as sole product 7-methyl-1:2:3:4-tetrahydroquinoline, b. p.  $130\text{--}132^\circ/12$  mm. (benzoyl derivative, m. p.  $70\text{--}72^\circ$ ; picrate, m. p.  $153\text{--}154^\circ$ ; hydrochloride, m. p.  $175^\circ$ ; the acetyl derivative is a liquid).

4-Methylquinoline yields a mixture of 4-methyl-1:2:3:4-tetrahydroquinoline, b. p.  $130^\circ/12$  mm. (benzoyl derivative, m. p.  $129^\circ$ ) and 4-methyl-5:6:7:8-tetrahydroquinoline, a colourless liquid, b. p.  $129^\circ/11$  mm. (hydrochloride, m. p.  $203\text{--}204^\circ$ ; picrate, m. p.  $170^\circ$ ; methiodide, m. p.  $183^\circ$  after darkening at  $179^\circ$ ). The latter substance is smoothly reduced by sodium and alcohol to 4-methyldecahydroquinoline, a colourless liquid, b. p.  $105^\circ/11$  mm. (hydrochloride, m. p.  $205^\circ$ ; picrate, m. p.  $159^\circ$ ; phenylthiocarbamide derivative, m. p.  $105^\circ$ ; methiodide,  $C_{12}H_{24}NI$ , m. p.  $235^\circ$ ).

3-Methylquinoline is obtained conveniently from *o*-aminobenzaldehyde and propaldehyde at 120–130°. It is hydrogenated to a mixture of 3-methyl-1:2:3:4-tetrahydroquinoline, a colourless liquid, b. p. 116–118°/10 mm. (benzoyl derivative, m. p. 84°; hydrochloride, m. p. 207°; picrate, m. p. 155°; the nitroso-compound is a liquid) and 3-methyl-5:6:7:8-tetrahydroquinoline, b. p. 126–127°/17 mm. (the hydrochloride does not solidify; chloroplatinate, decomp. 219°; picrate, m. p. 171°; methiodide, m. p. 162°). Sodium and alcohol convert the latter compound into 3-methyldecahydroquinoline, b. p. 125–127°/15 mm., m. p. 70–71° (picrate, m. p. 75°; hydrochloride, m. p. 218° after softening at 210°; the nitroso- and benzoyl derivatives are liquid).

2-Methylquinoline yields 2-methyl-1:2:3:4-tetrahydroquinoline, b. p. 115–116°/12 mm., and 2-methyl-5:6:7:8-tetrahydroquinoline, a colourless liquid, b. p. 101–104°/12 mm.,  $d_4^{20}$  1.0000 (picrate, lemon-yellow needles, m. p. 154°; hydrochloride, m. p. 164°; very hygroscopic methiodide, m. p. 118°). Temperature and concentration of the solution appear to have little influence on the course of the hydrogenation.

2:3-Dimethylquinoline, m. p. 68°, is obtained by Pfizinger's method by the decarboxylation of 2:3-dimethylcinchononic acid derived from isatin and methyl ethyl ketone. The crude acid contains small amounts of 2-ethylcinchononic acid, m. p. 174°, since, when converted into its silver salt and subsequently treated with methyl iodide, it gives a readily separable mixture of methyl 2:3-dimethylcinchonate, m. p. 120–121°, and methyl 2-ethylcinchonate, b. p. 176–178°/13 mm., m. p. 38°. The dimethyl derivative is hydrogenated to a mixture of 2:3-dimethyl-1:2:3:4-tetrahydroquinoline, a mobile liquid, b. p. 127–128°/13 mm.,  $d_4^{20}$  1.0048 (benzoyl derivative, slender, colourless crystals, m. p. 94–95°; hydrochloride, m. p. 154°; picrate, m. p. 161°; nitroso derivative, yellow platelets, m. p. 56°) and 2:3-dimethyl-5:6:7:8-tetrahydroquinoline, m. p. 38°, b. p. 125–126°/14 mm. (very hygroscopic hydrochloride, m. p. 192°; picrate, m. p. 169°; methiodide, m. p. 117°). The latter base is transformed by sodium and alcohol into 2:3-dimethyldecahydroquinoline, a mobile liquid, b. p. 95–97°/11 mm.,  $d_4^{20}$  0.9152 (the picrate and nitroso-compounds are liquid; the hydrochloride does not melt below 280°; methiodide, m. p. 199°).

2:4-Dimethylquinoline gives 2:4-dimethyl-1:2:3:4-tetrahydroquinoline, b. p. 125–127°/12 mm., and, mainly, 2:4-dimethyl-5:6:7:8-tetrahydroquinoline, b. p. 122–123°/12 mm. (picrate, m. p. 144°; hydrochloride, m. p. 195°; methiodide, m. p. 163° after darkening at 157°). 2:4-Dimethyldecahydroquinoline has b. p. 96–97°/12 mm. (picrate, m. p. 141–145°; hydrochloride, slender needles; methiodide, m. p. 210° after softening at 200°; the nitroso-derivative is a yellow liquid).

H. W.

5:6:7:8-Tetrahydroquinolines and their Derivatives.  
III. Tricyclic Compounds. JULIUS VON BRAUN, ADOLF  
PETZOLD, and ADAM SCHULTHEISS (*Ber.*, 1923, 56, [B], 1347–  
1350).—The presence of methyl groups in the pyridine portion of

the quinoline molecule has been shown (preceding abstract) to cause catalytic hydrogenation to occur to a greater extent in the benzenoid portion of the molecule. The same effect is observed when the substituents are themselves united in a ring, as is shown by experiments with tetrahydroacridine and 2:3-trimethylenequinoline.

Tetrahydroacridine, m. p. 54°, which is readily prepared from isatin and cyclohexanone, is hydrogenated at 150° to a mixture of

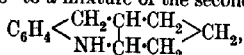
α-octahydroacridine,  $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} C_6H_{10}$ , m. p. 84°, b. p. 183°/12 mm. (benzoyl derivative, m. p. 104°) and s-octahydroacridine,  $C_6H_8 \begin{smallmatrix} CH \\ \diagup \quad \diagdown \\ N \end{smallmatrix} C_6H_8$ , colourless crystals, m. p. 69°, b. p. 175°/17 mm.

(the hydrochloride is liquid; chloroplatinate, red needles, m. p. 199—200°; picrate, m. p. 195°; methiodide, m. p. 159°). The symmetrical octahydro-base is reduced by sodium and alcohol to

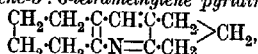
perhydroacridine,  $C_6H_{10} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} C_6H_{10}$ , b. p. 140°/14 mm., m. p.

80° (the hydrochloride does not melt below 300°; picrate, m. p. 167°; nitroso-derivative, m. p. 217°; methiodide,  $C_{15}H_{28}NI$ , m. p. 266°).

2:3-Trimethylenequinoline, from isatin and cyclopentanone, is hydrogenated at 170° to a mixture of the secondary base,



b. p. 169—171°/18 mm. (benzoyl derivative, m. p. 157°; hydrochloride, m. p. 143°; picrate, m. p. 154°; nitroso-derivative, m. p. 154°) and 2:3-trimethylene-5:6-tetramethylene pyridine,



b. p. 160—161°/17 mm. (hydrochloride, m. p. 91°; picrate, yellow needles, m. p. 160°). Reduction with sodium and alcohol converts the base into the perhydrogenated amine,  $C_{12}H_{21}N$ , a colourless, mobile liquid, b. p. 140—142°/17 mm. (picrate, small, yellow needles, m. p. 171°; hydrochloride, decomp. 255—258°; the nitroso-derivative could not be caused to crystallise).

H. W.

#### 5-Methyl-1:2:3:4-tetrahydroquinoline and its Fission.

JULIUS VON BRAUN and THEO KÜHLEIN (*Ber.*, 1923, 56, [B], 1351—1352).—The replacement of the chlorine atom in 8-chloro-5-methylquinoline by hydrogen cannot be effected smoothly by hydriodic acid or tin and hydrochloric acid. The base is, however, quantitatively converted by sodium and alcohol into 5-methyl-1:2:3:4-tetrahydroquinoline, b. p. 130—131°/14 mm. (hydrochloride, m. p. 228°; picrate, m. p. 156°; nitroso-derivative, m. p. 66—67°; benzoyl compound, m. p. 121°). The benzoyl derivative is converted by phosphorus pentachloride into 3-methyl-2-γ-chloropropylbenzamide, m. p. 102—103°.

H. W.

**Pictet's Synthesis of Tetrahydroisoquinoline.** HEISABURO KONDO and ELI OCHIAI (*J. Pharm. Soc. Japan*, 1923, No. 495, 313—319).—Pictet and Spengler (A., 1911, i, 750) synthesised tetrahydroisoquinoline by warming a mixture of phenylethylamine and aldehyde in the presence of concentrated hydrochloric

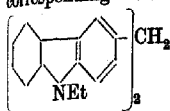
acid. The authors find that as pointed out by Decker and Becker, (A., 1913, i, 291), the reaction is not simple. Phenylethylamine hydrochloride (100 g.) is dissolved in 600 g. of concentrated hydrochloric acid, heated on a water-bath, 100 g. of dimethoxymethane are gradually added, and the mixture is heated during ten hours. After heating under reduced pressure to remove hydrochloric acid the residue is dissolved in water, rendered alkaline with sodium hydroxide, and extracted first with ether and then with chloroform. The former extract on fractionation yielded (1) 49 g. distilling between 70° and 120°/6 mm. (mainly 84°/6 mm.), and (2) 18 g. distilling between 200° and 250°/6 mm. (mainly 210°/6 mm.). When treated with sodium nitrite and reduced with tin and hydrochloric acid, (1) yielded  $\beta$ -phenylethyl chloride and a small quantity of tetrahydroisoquinoline. The fraction (1) is therefore composed mainly of unchanged phenylethylamine with a small quantity of tetrahydroisoquinoline. When acidified with hydrochloric acid and concentrated, (2) yielded white crystals of *di*-( $\beta$ -phenylethylamino)-methane hydrochloride, m. p. above 300°. It forms double salts with chloroplatinic acid, dichromate, mercuric chloride, etc., all melting above 380°. The *chloraurate*, yellow needles, has m. p. 118–120°. The free base,  $\text{CH}_2(\text{NH}-\text{C}_2\text{H}_5\text{Ph})_2$ , forms white needles, m. p. 150–151°, gives Liebermann's secondary amine reaction and easily absorbs carbon dioxide. The *diacetyl* derivative, silky needles, has m. p. 190°. From the chloroform solution a base was also obtained as a yellowish-brown, amorphous powder, which is identical with that obtained by heating a mixture of phenylethylamine hydrochloride, methylal, and hydrochloric acid in a sealed tube at 130°, but its nature is not yet clear. K. K.

**The Relative Stability of Cyclic Bases. IX.** JULIUS VON BRAUN (*Ber.*, 1923, 56, [B], 1570–1573).—It has been shown previously (A., 1916, i, 421) that the introduction of methyl groups into the 2-, 3-, or 4-positions of tetrahydroquinolinium chloride has little influence on the stability of this compound towards sodium amalgam. Similar observations are now recorded with the methylated 3-ethyl- and 3-amyl-tetrahydroquinolinium chlorides, from which it follows that the stability of the ring is not greatly influenced by the magnitude of the alkyl residue. When chlorides which contain two different alkyl groups attached to the nitrogen atom are acted on by sodium amalgam, it is found that it is the smaller of the two groups which is removed; this is established experimentally in the case of *N*-ethylhexahydrocarbazole methochloride.

The quaternary methiodide of 3-ethyltetrahydroquinoline is converted into the corresponding chloride, which is reduced by sodium amalgam; the product is treated with formaldehyde and hydrochloric acid, whereby ultimately  $\alpha$ -phenyl- $\beta$ -dimethylamino-methyl-*n*-butane,  $\text{CH}_2\text{Ph}-\text{CH}(\text{CH}_2\text{NMe}_2)-\text{CH}_2\text{Me}$ , b. p. 112–114°/12 mm., is obtained in 70% yield. It forms a non-crystalline *hydrochloride*, a *picrate*, thick, rhombic rods, m. p. 132°, and a *methiodide*, m. p. 155–160°, according to the rate of heating. In a

similar manner, the quaternary methiodide of 3-amyltetrahydroquinoline is converted into  $\alpha$ -phenyl- $\beta$ -dimethylaminomethylheptane,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CH}_2\text{NMe}_2)\cdot\text{C}_6\text{H}_{11}$ , b. p. 147–149°/11 mm. (the *picrate*, m. p. 97°, the non-crystalline *hydrochloride*, and the *methiodide*, m. p. 95°, are described).

Ethylhexahydrocarbazole methiodide is converted into the corresponding chloride and reduced with sodium amalgam; the



mixture of bases is treated with formaldehyde and hydrochloric acid, whereby the *compound* (annexed formula), m. p. 89–90° (*dimethiodide*, m. p. 83–84°), is obtained in 60% yield. (The identity of the compounds is established by their production from an authentic specimen of ethylhexahydrocarbazole.) The volatile bases which remain after treatment of the crude mixture with formaldehyde are separated by methyl iodide into *o*-cyclohexylmethyl ethylaniline,  $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_4\cdot\text{NMeEt}$ , b. p. 147–149°/12 mm. (*picrate*, m. p. 164°) and *o*-phenylcyclohexylmethyl ethylamine methiodide,  $\text{C}_{16}\text{H}_{28}\text{NI}$ , m. p. 186°. H. W.

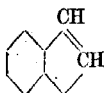
#### The Action of Magnesium Propyl Bromide on Quinoline

**Methiodide. Stereochemistry of Tervalent Nitrogen.** JAKOB MEISENHEIMER and MAX SCHÜTZE (*Ber.*, 1923, 56, [B], 1353–1362).—In a recent communication, Freund and Kessler (*A.*, 1919, i, 283) have described several pairs of stereoisomeric 1-methyl-2-alkyltetrahydroquinolines the occurrence of which is attributed to the presence of an asymmetric nitrogen and carbon atom. The authors' experience has led them to the conclusion that the saturated, tervalent nitrogen atom can only function as an asymmetric centre in very unusual cases. Since, moreover, the asymmetry does not disappear according to Freund and Kessler when methyl iodide is added to the isomerides, the authors have repeated the work, which is found to be erroneous. The results obtained are due to the attempt of Freund and Kessler to purify 1-methyl-2-propyl-1:2-dihydroquinoline by distillation under atmospheric pressure; in the circumstances, it becomes decomposed to a very considerable extent into methane and 2-propylquinoline, whilst a small quantity is reduced to the tetrahydro-derivative; the residue remains unchanged or is decomposed in other unexplained directions. Freund and Kessler's 1-methyl-2-propyl-1:2-dihydroquinoline is therefore a mixture of much 2-propylquinoline, little 1-methyl-2-propyl-1:2:3:4-tetrahydroquinoline and other compounds with the unaltered dihydroquinoline.

1-Methyl-2-propyl-1:2-dihydroquinoline, b. p. 152°/13 mm., is prepared in 60–70% yield according to the method of von Braun and Aust (*A.*, 1915, i, 586); the corresponding *picrate* has m. p. 72° but is so unstable in solution that it cannot be recrystallised. The base is decomposed when boiled under atmospheric pressure, yielding mainly 2-propylquinoline, a pale, greenish-yellow liquid, b. p. 130–131°/10 mm., together with small amounts of 1-methyl-2-propyl-1:2:3:4-tetrahydroquinoline, which is identified as the *picrate*, m. p. 123°. 2-Propylquinoline methiodide is a pale yellow,

crystalline powder, m. p. 181°, which is completely decomposed by repeated crystallisation from alcohol. 2-Propyltetrahydroquinoline, b. p. 140—140.5°/10 mm. [von Braun and Aust (*loc. cit.*) give b. p. 152°/20 mm.], is prepared by the reduction of 2-propylquinoline with tin and hydrochloric acid. The hydrochloride, colourless needles, m. p. 221—222° (220°) and the benzoyl derivative, m. p. 102° (97°) are described. (The figures placed within brackets are the data of von Braun and Aust.) The picrate (m. p. 143°) separates from water (+H<sub>2</sub>O) as a brown oil which gradually solidifies, m. p. 56—60°, from toluene (+0.5 C<sub>6</sub>H<sub>6</sub>) in needles, m. p. 115°, and from alcohol or ether in reddish-brown or orange-coloured plates, m. p. 125°. Reduction of 1-methyl-2-propyl-1:2-dihydroquinoline is not smoothly effected by tin and hydrochloric acid (cf. von Braun and Aust, *loc. cit.*), but may be readily performed with sodium and alcohol, thus yielding 1-methyl-2-propyl-1:2:3:4-tetrahydroquinoline, a pale yellow liquid, b. p. 144.5°/10 mm. (151—157°/20 mm.). 1-Methyl-2-propyl-1:2:3:4-tetrahydroquinoline methiodide forms coarse, colourless crystals, which have m. p. 180—200° (decomp.) according to the mode of heating.

1-Methyl-2-propyl-1:2-dihydroquinoline picrate is decomposed in boiling alcoholic solution; one-third of it is transformed into 1-methyl-2-propylquinolinium picrate, yellow needles, the constitution of which is established by its formation from the corresponding methiodide and picric acid, a second third is converted into the indole picrate (? annexed formula), reddish-brown leaflets, m. p. 122°, whereas the remaining third becomes resinified.

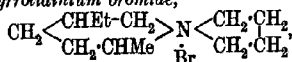


H. W.

**Cyclic Di-imines and their Decomposition. II.** JULIUS VON BRAUN, GEORG LEMKE, and ANNEMARIE NELKEN (*Ber.*, 1923, 56, [B], 1564—1569).—A comparatively easy method for the preparation of pyrrolidine is based on the interaction of 2-methyl-5-ethylpiperidine (copellidine) with  $\alpha$ , $\beta$ -dibromobutane, transformation of the product into the corresponding cyclic di-imine, and fission of the latter.

Technical copellidine is a mixture of two racemic, *cis-trans*-isomerides which have been designated copellidine and isocopellidine, respectively; for these the authors prefer the designation A- and B-copellidine, and reserve the term "copellidine" for the mixture of bases. The isomerides are readily separated from one another by utilising the observation that A-copellidine hydrochloride, in contrast to the B-isomeride, is difficultly soluble in acetone. For the present purpose, the mixture of bases may be employed, but the experimental difficulties are greater than when either of the homogeneous isomerides is used.

A-Copellidylpyrrolidinium bromide,

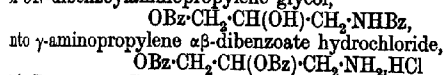


a very hygroscopic substance, m. p. 195°, is prepared by the action

of *A*-copellidine on  $\alpha\beta$ -dibromobutane in boiling alcoholic solution; the corresponding *chloride*, an extremely hygroscopic, crystalline mass, and the *chloroplatinate*, m. p.  $242^\circ$  (decomp.) are described. *B*-Copellidylpyrrolidinium bromide has m. p.  $176-177^\circ$ ; the corresponding *chloride* is extremely hygroscopic; the *chloroplatinate* has decomp.  $234^\circ$ . The bromides are converted by treatment with aqueous ammonia (25%) at  $180^\circ$  during twenty-four hours into a mixture of pyrrolidine (the yield is about 66% of that theoretically possible) and the corresponding di-imine. *A*-Methyl-ethylbis-pentamethyleneimine,  $\text{CH}_2 < \begin{matrix} \text{CHEt} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{matrix}$ , is an almost colourless, fairly mobile liquid, b. p.  $132-136^\circ/12$  mm. The *hydrochloride* and the *picrate* are non-crystalline. The *picrolonate* has m. p.  $174-175^\circ$ . The *benzenesulphonyl* derivative could not be caused to crystallise. Treatment of the base with alkali and methyl iodide results in the production of a quaternary iodide which rapidly alters on exposure to air and is therefore converted into the *chloride*, from which the *chloroplatinate*,  $\text{C}_{16}\text{H}_{38}\text{N}_2\text{Cl}_2\text{Pt}$ , a yellow, crystalline powder, m. p.  $254^\circ$ , and the *chloroaurate*, m. p.  $223-225^\circ$ , are prepared. *B*-Methylethylbis-pentamethyleneimine resembles exactly the *A*-compound in appearance, odour, and boiling point. The *hydrochloride*, *picrate*, and *benzenesulphonyl* derivative are non-crystalline; the *picrolonate* has m. p.  $144^\circ$ . The *chloroplatinate* obtained from the hygroscopic, quaternary iodide has m. p.  $252^\circ$ , whereas the *chloroaurate* has m. p.  $216-218^\circ$ .

H. W.

**Displacement of Acyl Groups from Nitrogen to Oxygen in the Cases of Amino-alcohols.** MAX BERGMANN and ERWIN BRAND (*Ber.*, 1923, 56, [B], 1280-1283).—The transformation of *ON*-dibenzoylamino-propylene glycol,



(cf. Bergmann, Brand, and Dreyer, *A.*, 1921, i, 444), has been examined in greater detail.

The conversion is most conveniently effected by means of thionyl chloride at the atmospheric temperature whereby an intermediate product, probably 2-phenyl-5-benzoxymethyl-oxazoline hydrochloride,  $\text{OBz} \cdot \text{CH}_2 \cdot \text{CH} < \begin{matrix} \text{CH}_2 \cdot \text{N} \\ | \\ \text{O} - \text{CPh} \end{matrix}$ ,  $\text{HCl}$ , m. p.  $130-131^\circ$ ,

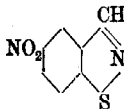
can be isolated. It is transformed by water at  $18^\circ$  into  $\gamma$ -aminopropylene  $\alpha\beta$ -dibenzoate hydrochloride or the free base. The following salts of the oxazoline derivative are described: the *hydrogen sulphate*,  $\text{C}_{17}\text{H}_{17}\text{O}_4\text{N}_2\text{H}_2\text{SO}_4$ , m. p.  $77-78^\circ$ ; the *normal sulphate*, m. p.  $152-153^\circ$  (decomp.), and the *picrate*, m. p. about  $105^\circ$ .

*ON*-Dibenzoylamino-propylene glycol is transformed by phosphoryl chloride in the presence of anhydrous chloroform into a compound,  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{NPCl}_2$ , needles, m. p.  $102-103^\circ$ . It is converted by pyridine into the oxazoline derivative.

H. W.

**Derivatives of Benz-4:5-isothiazole.** K. FRIES and G. BROTHUHN (*Ber.*, 1923, 56, [B], 1630—1633). Derivatives of benz-4:5-isothiazole are obtained by the action of ammonia on arylsulphur halides which contain an aldehydic or ketonic group in the neighbourhood of the sulphur atom.

4:4'-Dinitro-2:2'-dialdehydodiphenyl disulphide, coarse, pale yellow needles, m. p. 256°, is prepared by the action of sodium disulphide on a solution of 2-chloro-5-nitrobenzaldehyde in alcohol. It is converted by prolonged treatment with a solution of bromine in carbon tetrachloride at 100° into 4-nitro-2-aldehydophenylsulphur bromide,  $\text{CHO}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{SBr}$ , m. p. 171°, which is transformed by dimethylaniline dissolved in benzene into 4-nitro-2-aldehydo-4'-dimethylaminodiphenyl sulphide,  $\text{CHO}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , yellowish-red, prismatic crystals, m. p. 164° (hydrochloride, colourless, cubic crystals, m. p. 197° (decomp.)). When a solution of the sulphur bromide in benzene is heated with concentrated aqueous ammonia, 5-nitrobenz-4:5'-isothiazole (annexed formula), colourless needles, m. p. 149°, is obtained. 4-Nitro-2-aldehydophenylsulphur bromide is converted by aniline in the presence of benzene into 5-nitro-2-phenylbenz-4:5'-

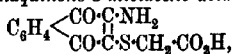


isothiazolium bromide,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{CH} \\ \text{S} \end{smallmatrix}\rangle\text{NPh}\cdot\text{Br}$ , decomp. about 240°, which is transformed by concentrated hydrochloric acid into the corresponding chloride, pale yellow, prismatic crystals, m. p. about 228° (decomp.). H. W.

**2:3-Dichloro-1:4-naphthaquinone.** K. FRIES and P. OCHWAT (*Ber.*, 1923, 56, [B], 1291—1304; cf. Fries and Kerkow, A., 1922, i, 577).—The replaceability of the halogen atoms of 2:3-dichloro-1:4-naphthaquinone by a variety of other groups has been examined; in certain cases one chlorine atom appears to be far more easily displaced than the other, whereas in other cases both atoms are replaced.

3-Chloro-2-amino-1:4-naphthaquinone is readily obtained in the pure condition by the gradual addition of concentrated ammonia to a suspension of 2:3-dichloro-1:4-naphthaquinone in boiling alcohol; the corresponding acetyl derivative forms brownish-red leaflets, m. p. 219°. The amine is converted by boiling acetic anhydride in the presence of a little concentrated sulphuric acid into 2-methyl-ββ-naphthorazole-4:9-quinone,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{N} \\ \text{CO}\cdot\text{C}\cdot\text{O} \end{smallmatrix}\rangle\text{CMe}$ ,

brownish-yellow crystals, m. p. 317° (diacetate, colourless needles, m. p. 222°). It is transformed by the successive action of sodium sulphide and methyl sulphate into 2-amino-3-methylthiol-1:4-naphthaquinone, brownish-red needles, m. p. 132°, which loses the methylthiol group under the influence of hydrogen peroxide. 2-Amino-1:4-naphthaquinone-3-thiolacetic acid,



brown leaflets, m. p. 220° (decomp.), is prepared by the addition

of sodium chloroacetate solution to the sodium salt of amino-thionaphthaquinone. When a solution of the acid in glacial acetic acid is boiled it is converted into 3:5:10-triketo-2:3-dihydro-naphthathiazine,  $C_8H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{C} \cdot \text{S} \cdot \text{CH}_2 \end{smallmatrix}$ , dark brown needles, m. p. 260° (decomp.), which is converted by zinc dust and boiling acetic anhydride into 3-keto-5:10-diacetoxy-2:3-dihydro-1:4-naphthathiazine,  $C_8H_4 \begin{smallmatrix} \text{C}(\text{OAc}) \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ \text{C}(\text{OAc}) \cdot \text{C} \cdot \text{S} \cdot \text{CH}_2 \end{smallmatrix}$ , colourless leaflets, m. p. 270° (decomp.).

The addition of 2:3-dichloro-1:4-naphthaquinone to the product of the action of sodium sulphide on 3-chloro-2-anilino-1:4-naphthaquinone leads to the production of 6-phenyldinaphthathiazine-5:7:12:14-diquinone (annexed formula), small, brown crystals, which is converted by boiling nitrobenzene or, preferably, by nitric acid (d 1.4) in the presence of into 12-phenyldibenzcarbazole-5:6:11:13-diquinone (annexed formula), slender, yellow needles, m. p. above 400°. The latter compound is converted by zinc dust and boiling acetic anhydride into 12-phenyl-5:6:11:13-tetra-acetoxydibenzcarbazole, yellow crystals, m. p. 275° (decomp.). The carbazolidiquinone is reduced by an excess of stannous chloride in the presence of glacial acetic acid to 12-phenyldibenzcarbazole-5:6-quinone, coarse, dark brown, lustrous crystals, m. p. above 360°.

3-Chloro-2-p-chloroanilino-1:4-naphthaquinone, red, prismatic crystals, m. p. 266°, is obtained from 2:3-dichloro-1:4-naphthaquinone and p-chloroaniline and is converted in a similar manner into the following series of derivatives: 6-p-chlorophenyldinaphthathiazine-5:7:12:14-diquinone, brown, prismatic crystals, m. p. above 360°; 12-p-chlorophenyldibenzcarbazole-5:6:11:13-diquinone, yellow leaflets, m. p. above 360°; 13-p-chlorophenyl-5:6:11:13-tetra-acetoxydibenzcarbazole, small, yellow crystals, m. p. above 360°; 12-p-chlorophenyldibenzcarbazole-5:6-quinone, coarse, brown crystals, m. p. above 360°.

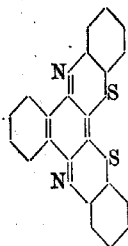
2:3-Diazido-1:4-naphthaquinone,  $C_8H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N}_3 \\ \text{CO} \cdot \text{C} \cdot \text{N}_3 \end{smallmatrix}$ , m. p. 136°, appears to be the sole product of the action of sodium azide on a suspension of dichloronaphthaquinone in boiling alcohol, whereas under similar conditions sodium acetate yields 3-chloro-2-acetoxy-1:4-naphthaquinone, slender, yellow needles, m. p. 98°.

2-Amino-3-thiol-1:4-naphthaquinone and chloroaminonaphthaquinone yield the compound (annexed formula), brownish-yellow crystals, m. p. above 360°.

g g\* 2

*o*-Nitroaniline,  $\beta$ -aminoanthraquinone, and 3-chloro-2-aminonaphthaquinone could not be caused to react with dichloro- $\alpha$ -naphthaquinone. The latter substance does not appear to react with benzene in the presence of aluminium chloride.

2 : 3-Dichloro-1 : 4-naphthaquinone reacts with *o*-nitrothiophenol to give 2 : 3-di-*o*-nitrophenylthiol-1 : 4-naphthaquinone, slender, cinabar-red needles, m. p. 253°, which is transformed by stannous chloride in the presence of glacial acetic acid into 1 : 4-dihydroxy-2 : 3-di-*o*-nitrophenylthiolnaphthalene, slender, almost colourless needles, m. p. 233° (diacetate, slender needles, m. p. 217°). The protracted action of stannous chloride and glacial acetic acid on di-*o*-nitrophenylmercaptanaphthaquinone leads to the production of the compound (annexed formula), dark red needles, m. p. above 360° (the additive compound with tin chloride is also described). 3-Anilino-2-*o*-nitrophenylthiol-1 : 4-naphthaquinone, bluish-red leaflets, m. p. 216°, is



prepared by the action of the requisite quantity of aniline on the di-*o*-nitrophenylmercapto-derivative.

[With W. PENSE].—The following substances have been prepared from chloranil: Tetra-*o*-nitrophenylthiol-*p*-benzoquinone, brownish-yellow crystals which explode violently when heated. 2 : 5-Di-anilino-3 : 6-di-*o*-nitrophenylthiol-*p*-benzoquinone, m. p. above 360°, obtained by the action of aniline on the preceding compound. 2 : 5-Dichloro-3 : 6-diaido-*p*-benzoquinone, coarse, prismatic crystals which explode violently when heated previous to melting. Tetra-azido-*p*-benzoquinone, brownish-yellow crystals which are exceedingly explosive.

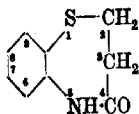
H. W.

#### Seven-membered Rings containing Sulphur and Nitrogen.

FRITZ MAYER and CARL HORST (*Ber.*, 1923, 56, [B], 1415–1423).—

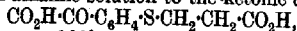
A series of compounds containing the heptathiazine ring,  $\begin{matrix} \text{C-S-C} \\ \diagup \quad \diagdown \\ \text{C-N-C} \end{matrix}$ , is described.

$\beta$ -*o*-Nitrophenylthiolpropionic acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 145°, is prepared in 71% yield by the action of *o*-nitrophenyl mercaptan on a solution of sodium  $\beta$ -chloropropionate; the methyl ester, pale yellow needles, m. p. 76°, and the ethyl ester, greenish-yellow leaflets, m. p. 69°, are described. The acid is reduced by ferrous sulphate and ammonia to  $\beta$ -*o*-aminophenylthiolpropionic acid, coarse, colourless needles, m. p. 84°; the hydrochloride, colourless needles, m. p. 189°, and the ethyl ester hydrochloride, colourless needles, m. p. 144°, are described. The ethyl ester is a liquid which cannot be distilled.  $\beta$ -*o*-Hydroxyphenylthiolpropionic acid has m. p. 86–88°. The amino acid is almost quantitatively converted at 150–190° into 4-ketotetrahydro-1 : 5-heptabenzthiazine (annexed formula), colourless leaflets or needles, m. p. 215–216°, which can also be obtained from the hydrochloride of the acid at 190–200° or by distillation of the ethyl



ester. The substance immediately dissolves in concentrated or dilute solutions of alkali, giving an odour of mercaptan; it is converted by concentrated hydrochloric acid at  $110^{\circ}$  into the hydrochloride of the amino-acid.

$\beta$ -o-Cyanophenylthiolpropionic acid, m. p.  $92-93^{\circ}$  after softening at  $87^{\circ}$ , is obtained from the corresponding amino-acid in the usual manner. It is converted by concentrated hydrochloric acid at  $100^{\circ}$  into  $\beta$ -o-carboxyphenylthiolpropionic acid, m. p.  $140^{\circ}$  after softening at  $185^{\circ}$ . The latter acid can also be obtained in the following manner: thionaphthenquinone is condensed with  $\beta$ -chloropropionic acid in alkaline solution to the ketonic acid,



yellow leaflets, m. p.  $138^{\circ}$  (oxime, colourless needles, m. p.  $92^{\circ}$ ), which is then oxidised by hydrogen peroxide in the presence of sodium hydroxide to the desired compound.

The heptabenzthiazine is converted by sulphuryl chloride in the presence of benzene into 2(?) -chloroketotetrahydroheptabenzthiazine, pale yellow crystals, decomp.  $138-143^{\circ}$ , which is transformed by boiling ethyl alcohol into 2(?) -ethoxyketotetrahydroheptabenzthiazine, slender, colourless needles, m. p.  $172-173^{\circ}$ , and by methyl alcohol into 2(?) -methoxy-4-ketotetrahydroheptabenzthiazine, colourless needles, m. p.  $175-176^{\circ}$ . Ketoheptabenzthiazine-2(?) -thiolacetic acid has m. p.  $209-210^{\circ}$ . In the presence of chlorobenzene, the heptabenzthiazine is transformed by the requisite quantity of sulphuryl chloride into 2(?) -dichloroketotetrahydroheptabenzthiazine, colourless needles, m. p.  $254-255^{\circ}$  (the sodium salt,  $\text{C}_6\text{H}_5\text{ONCl}_2\text{SNa}$ , colourless needles, decomp.  $135^{\circ}$ , is described). The action of acetic anhydride on the benzheptathiazine or on  $\beta$ -o-aminophenylthiohydraacrylic acid gives a substance, long colourless needles, m. p.  $87^{\circ}$ , the analyses of which do not appear to harmonise with those required by any simple derivative of the parent compound.  $\beta$ -o-Nitrophenylthiolpropionic acid is oxidised by potassium permanganate in alkaline solution to  $\beta$ -o-nitrophenylsulphonpropionic acid,  $\text{C}_6\text{H}_4\text{O}_6\text{NS}$ , colourless leaflets, m. p.  $144^{\circ}$  (ethyl ester, colourless needles, m. p.  $45^{\circ}$ ).  $\beta$ -o-Aminophenylsulphonpropionic acid, colourless needles, m. p.  $105^{\circ}$  (hydrochloride, colourless, lustrous needles, m. p.  $184-186^{\circ}$ , after previous softening), is prepared by the reduction of the nitro-acid with ferrous sulphate and ammonia. It is converted when heated above its melting point into ketotetrahydroheptabenzsulphazone,  $\text{C}_6\text{H}_4\cdot\left\langle\begin{smallmatrix} \text{SO}_2\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\right\rangle\text{CH}_2$ , colourless needles, m. p.

$246-247^{\circ}$ , which, however, is more conveniently prepared by oxidising the benzheptathiazine dissolved in glacial acetic acid with hydrogen peroxide. It is converted by concentrated hydrochloric acid at  $125^{\circ}$  into the hydrochloride of the amino-acid.

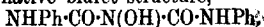
$\beta$ -4-Chloro-2-nitrophenylthiolpropionic acid crystallises in pale yellow needles, m. p.  $168-159^{\circ}$  (ethyl ester, pale yellow needles, m. p.  $77^{\circ}$ ). It is reduced to  $\beta$ -4-chloro-2-aminophenylthiolpropionic acid, coarse, colourless needles, m. p.  $90^{\circ}$  after softening at  $88^{\circ}$  (hydrochloride, colourless needles, m. p.  $162-163^{\circ}$ ). 7-Chloroketotetrahydroheptabenzthiazine, prepared by heating the amino-acid above its

melting point, crystallises in colourless needles, m. p. 117°, and is hydrolysed to the acid by concentrated hydrochloric acid. The action of acetic anhydride on the chloroheptathiazine and on the amino-acid gives the same product, colourless needles, m. p. 112–113° or 116°, which does not give readily interpreted results when analysed.

2(?) : 7-Dichloroketotetrahydroheptabenzthiazine, colourless needles, decomp. 207° after becoming yellow at 170°, is prepared in a not quite homogeneous condition by the action of sulphuryl chloride on the monochloro-compound dissolved in a mixture of benzene and chlorobenzene. It is converted by boiling ethyl alcohol into 7-chloro-2(?)-ethoxyketotetrahydroheptabenzthiazine, colourless needles, m. p. 180°.  $\beta$ -4-Chloro-2-nitrophenylsulphonpropionic acid, colourless leaflets, m. p. 183–184°, is prepared by the oxidation of the corresponding nitrothio-acid with permanganate. 7-Chloroketotetrahydroheptabenzsulphazone, obtained from the 7-chlorobenzthiazine and hydrogen peroxide, has m. p. 269° after softening at 260°.

H. W.

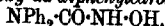
Reactions of  $\beta$ -Hydroxy- $\alpha$ -phenylcarbamide and of  $\beta$ -Hydroxy- $\alpha\alpha$ -diphenylcarbamide Interpreted from the Point of View of their Hydroxamic Acid Structures. CHARLES DEWITT HURD (*J. Amer. Chem. Soc.*, 1923, 45, 1472–1489).—Evidence is submitted which supports the hypothesis of Jones and Hurd (*A.*, 1922, i, 248), that if the radicle that wanders in a Beckmann conversion is potentially a free radicle, the change occurs with greater ease than otherwise. Thus derivatives of diphenylcarbamhydroxamic acid, the "free radicle" of which is  $\text{-NPh}_2$ , undergo rearrangement, but not derivatives of monophenylcarbamhydroxamic acid. The structure of carbanilido- $\beta$ -hydroxy- $\alpha$ -phenylcarbamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ , is discussed, this formula being preferred to the alternative biuret structure,



It is shown that in the formation of this compound, by boiling a solution of  $\beta$ -hydroxy- $\alpha$ -phenylcarbamide, an intermediate decomposition into hydroxylamine and phenylcarbimide does not occur, since phenylurethane is not produced when alcohol is used as a solvent, and aniline similarly remains unattacked, although phenylcarbimide reacts much more rapidly with aniline than with  $\beta$ -hydroxy- $\alpha$ -phenylcarbamide. The addition of phenylcarbimide to monohydroxamic acids apparently occurs at the  $\alpha$ - rather than at the  $\beta$ -hydroxylamino-position.

The benzoate of  $\beta$ -hydroxy- $\alpha$ -phenylcarbamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{O}\cdot\text{C}_6\text{H}_5$ , heavy, crystalline clumps, m. p. 179° (decomp.), forms a potassium salt which is stable in cold aqueous solution, but gives  $\alpha$ -diphenylcarbamide on boiling. The acetate, m. p. 121–123°, forms a potassium salt, m. p. 161°, and insoluble copper and silver salts. The acid sodium salt,  $[\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{OAc})]_2\text{HNa}$ , produced in alcoholic solution, is converted by means of cold or boiling water, or dilute sodium hydroxide solution, into carbanilido- $\beta$ -hydroxy- $\alpha$ -phenylcarbamide, and a compound, needles, m. p. 160–161°, which gives

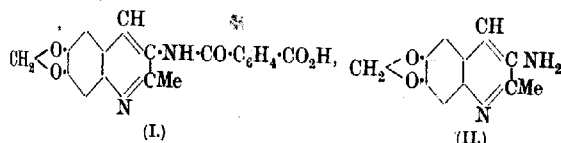
carbanilide- $\beta$ -hydroxy- $\alpha$ -phenylcarbamide when dissolved in concentrated sulphuric acid and poured into water. *Diphenylcarbamhydroxamic acid* ( $\beta$ -hydroxy- $\alpha\alpha$ -diphenylcarbamide),



colourless needles, m. p.  $134-134.5^\circ$  (decomp.), is prepared by the action of hydroxylamine on diphenylcarbamide chloride in methyl alcoholic or benzene solution, and gives an *acetate*, white needles, m. p.  $126.5-127^\circ$ , the *sodium* salt of which is formed in alcoholic solution, together with tetraphenylcarbazide,  $\text{CO}(\text{NH}\cdot\text{NPh}_2)_2$ , a product of rearrangement. The sodium salt suffers rearrangement, when left over-night in aqueous solution, with formation of diphenylamine and *as*-diphenylhydrazine. The latter is converted into diphenylamine by the prolonged action of water. The *benzoate* of diphenylcarbamhydroxamic acid gives a *sodium* salt in alcoholic solution. Since diphenylcarbamhydroxamic acid is not formed during the preparation of  $\beta$ -hydroxy- $\alpha\alpha$ -diphenylcarbamide from phenylcarbimide and phenylhydroxylamine, the latter shows no tendency to undergo fission between the phenyl and hydroxylamino-groups. In the absence of solvents, phenylcarbimide and benzhydroxamic acid form an *additive* compound, m. p.  $113-114^\circ$ , which is converted into *s*-diphenylcarbamide by heating at  $145^\circ$ , or by the action of alcoholic sodium methoxide. W. S. N.

**3-Amino- and 3-Hydroxy-quinolines.** S. BERLINGOZZI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 339-343).—With 6-aminopiperonaldehyde, acetylphthalimide and phenacylphthalimide react in the same way as with *o*-aminobenzaldehyde (cf. this vol., i, 482), the action of hydrochloric acid on the resulting products yielding 3-aminoquinoline derivatives, which are convertible into the corresponding 3-hydroxyquinoline derivatives by treatment with nitrous acid.

[With CLELIA NAPOLITANO.]—The compound (I), obtained by condensation of 6-aminopiperonaldehyde with acetylphthalimide in presence of sodium hydroxide, forms white needles, m. p. about  $250^\circ$  (decomp.).



**3-Amino-6 : 7-methylenedioxy-2-methylquinoline**, (II), obtained by boiling the preceding compound with 20% hydrochloric acid, forms pale yellow chips, m. p.  $210^\circ$ , and forms opalescent solutions in acids. The *acetyl* derivative,  $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$ , forms tufts of white needles, m. p.  $266-267^\circ$ , and the *picrate*, lemon-yellow prisms, m. p. about  $225^\circ$  (decomp.).

**3-Hydroxy-6 : 7-methylenedioxy-2-methylquinoline**,  $\text{C}_{12}\text{H}_9\text{O}_3\text{N}$ , prepared from the preceding compound by diazotisation, forms straw-yellow scales, m. p.  $284-285^\circ$  (decomp.), gives opalescent solutions

in acids, and with ferric chloride in alcoholic solution yields a blood-red coloration, which is destroyed by addition of hydrochloric acid. The compound obtained by condensation of 6-aminopiperonaldehyde with phenacylphthalimide in presence of sodium hydroxide, forms a white, microcrystalline powder, m. p. 265° (decomp.).

3-Amino-6:7-methylenedioxy-2-phenylquinoline crystallises in straw-yellow needles, m. p. 202°, and dissolves in acids, giving fluorescent solutions. The acetyl derivative, minute, lustrous, white needles, m. p. 234°, and the picrate, lemon-yellow needles, m. p. 217° (decomp.), were prepared.

3-Hydroxy-6:7-methylenedioxy-2-phenylquinoline,  $C_{17}H_{11}O_3N$ , forms lustrous, straw-yellow scales, m. p. 232°, yields opalescent solutions in acids, and in alcohol gives with ferric chloride an orange-red coloration, which is destroyed by hydrochloric acid.

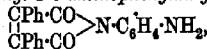
T. H. P.

Preparation of a Derivative of 5-Phenyl-5-ethylhydantoin. CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.P. 360688; from *Chem. Zentr.*, 1923, ii, 481—482).—5-Phenyl-5-ethylhydantoin

is acetylated, for example, by heating with acetic anhydride in the presence of a catalyst such as sulphuric acid. 1-Acetyl-5-phenyl-5-ethylhydantoin (annexed formula), thereby obtained, forms colourless crystals, m. p. 179°. The position of the acetyl group is inferred from the solubility of the compound in alkali.

G. W. R.

The Action of *o*-Phenylenediamine on Diphenylmaleic, Homophthalic, and Diphenic Anhydrides. A. BISTRZYCKI and KARL FÄSSLER (*Helv. Chim. Acta*, 1923, 6, 519—534).—The 1:2-*o*-benzoylene-1:3-benzdiazole obtained from phthalic anhydride and *o*-phenylenediamine (A., 1921, i, 456) has a yellow colour. To determine whether this colour is due to the type of fused ring system present in the compound, substances of similar character have been prepared by condensing *o*-phenylenediamine with other anhydrides of dibasic acids. Diphenylmaleic anhydride condenses with *o*-phenylenediamine in boiling alcohol to form 2:5-diketo-3:4-diphenyl-1-*o*-aminophenyldihydropyrrrole,



which forms orange, microscopic, prismatic needles, decomposing at 207—208°. It is a feebly basic substance and forms an acetyl derivative, yellow prisms or six-sided tables, m. p. 224°. When heated at 250°, the aminoanil loses 1 mol. of water, forming *ap*-diphenylacrylenebenzimidazole,  $\text{CPh}\cdot\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CPh}\cdot\text{C}\cdot\text{N}$ , brown, microscopic groups of needles, m. p. 186°. The same compound is

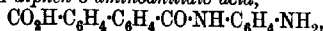
formed, but in poor yield, by heating together molecular proportions of *o*-phenylenediamine and diphenylmaleic anhydride. By alkalis it is readily converted into benzimidazole-2-*ap*-diphenylacrylic acid,  $\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CPh}\cdot\text{C}\cdot\text{N}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$ , crystallising with  $1\frac{1}{2}\text{H}_2\text{O}$

in colourless, microscopic crystals which when heated become orange, m. p.  $186^{\circ}$  (decomp.). From alcohol, the acid crystallises in long, colourless needles containing 1 mol. of the solvent. The *ethyl* ester forms colourless, microscopic needles which behave like the acid when heated, and the *anilide* forms microscopic needles decomposing at  $278^{\circ}$ .

Homophthalic anhydride combines with *o*-phenylenediamine in alcoholic solution to form, probably, *o*-carboxymethylbenz-*o*-amino-anilide,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , although the possibility remains that combination takes place at the other carboxyl group.

The compound forms colourless leaflets, and when heated at  $200^{\circ}$  loses water, forming 1:2-*o*-phenyleneacetyl-1:3-benzdiazole (annexed formula), yellow, short, microscopic prisms, decomposing at  $345^{\circ}$ . In acetic anhydride solution, it is blue and in concentrated sulphuric acid violet-brown. It can be regarded as a reduced isoquinoline derivative, and all attempts to open the new six-membered ring failed, the compound being remarkably stable.

Diphenic anhydride combines with *o*-phenylenediamine in boiling alcohol to form *diphen-o-aminoanilidic acid*,

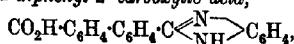


which forms colourless, rhombic tablets decomposing at  $165^{\circ}$ ; from alcohol, it crystallises with 1 mol. of solvent. The *silver*

salt forms a grey precipitate. When heated at  $150^{\circ}$ , the acid loses water, forming 2':1-*o*-benzoylene-2-phenyl-1:3-benzdiazole (annexed formula), which forms colourless, microscopic needles, m. p.  $177\text{--}178^{\circ}$ . The compound can be prepared in good yield by melting together diphenic anhydride and *o*-phenylenediamine and heating at  $150^{\circ}$ . It contains a new

seven-membered ring, and, unlike the above compounds containing a six- or five-membered ring condensed with the benzdiazole ring, it is colourless. The new ring is readily ruptured by alkali, and in this respect resembles the 5-membered ring of the above diphenylmaleic derivative.

*Benziminazole-2-diphenyl-2'-carboxylic acid*,



forms colourless, flat prisms which melt at  $206\text{--}207^{\circ}$  and lose water to form again the above seven-membered ring compound. The *silver* salt is white and but slightly sensitive to light. The *ethyl* ester forms short, flat, microscopic prisms, decomposing at  $143^{\circ}$ ; the *amide*, colourless, flat prisms, decomposing at  $227^{\circ}$ ; the *anilide*, rhombic tablets, decomposing at  $248^{\circ}$ ; the *phenylhydrazide*, microscopic rosettes of leaflets, decomposing at  $157^{\circ}$ . These amido-derivatives are all formed by the action of the base on the above benzoylene-phenylbenzdiazole. *N-o-Acetamido-phenyl diphenimide*,  $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , forms colourless, microscopic

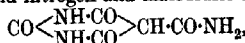
prisms decomposing at 233°. It is formed when the primary product of combination of diphenic anhydride and *o*-phenylenediamine is acetylated.

E. H. R.

**The Action of Carbamazide on Malonic Ester and on Barbituric Acid.** TH. CURTIUS (*Ber.*, 1923, 56, [B], 1577—1583).—The action of carbamazide on ethyl malonate and barbituric acid occurs in two directions. On the one hand, the azide loses hydrazoic acid and leaves a residue of isocyanic acid, which is isolated as cyanuric acid or as urazole, whereas, on the other hand, it loses nitrogen and the residue,  $\text{NH}_2\cdot\text{CO}\cdot\text{N}\cdot$ , unites with the partner in the reaction to yield substances containing the group  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}$ .

Urazole, m. p. 245°, cyanuric acid, *ethyl dicarbamidomalonate*,  $(\text{NH}_2\cdot\text{CO}\cdot\text{NH})_2\text{C}(\text{CO}_2\text{Et})_2$ , small, pointed, anisotropic platelets, m. p. 170°, and *ethyl carbamidomalonate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , colourless, anisotropic prisms, m. p. 145°, are obtained when carbamazide and ethyl malonate are warmed on the water-bath until evolution of nitrogen ceases. Urazole, cyanuric acid, and small amounts of a substance, m. p. 174° (decomp.), are the only products which could be isolated from the action of carbamazide and ethyl ethylmalonate.

Carbamazide and crystalline, hydrated barbituric acid when heated together yield nitrogen and malobiuric acid,



which is derived by the addition of nascent isocyanic acid to barbituric acid. The main product of the reaction, however, is a tile-red mass which is insoluble in all media and presumably contains bibarbituric acid. It is transformed by bromine water into a substance,  $\text{C}_6\text{H}_4\text{O}_7\text{N}_7$ , golden-yellow, anisotropic plates, dibromobibarbituric acid, and the hydrobromides of basic substances, which have not been investigated farther. The constitution of the compound  $\text{C}_6\text{H}_4\text{O}_7\text{N}_7$  has not been elucidated; it yields highly characteristic additive compounds with bases such as aniline, ammonia, and hydrazine. It is extremely sensitive to reducing agents and is converted by stannous chloride into the compound,  $\text{C}_6\text{H}_6\text{O}_8\text{N}_4$ , small, red needles (the corresponding *monohydrate* is described). The substance can also be obtained by the use of sulphurous acid and, in this case, the mother-liquors contain a compound,  $\text{C}_6\text{H}_5\text{O}_7\text{N}_6$ , large, colourless leaflets, decomp. 268°, which has feeble acidic properties and yields a highly characteristic, gelatinous silver salt. It reacts violently with hydrazine in aqueous solution, giving an acid,  $\text{C}_3\text{H}_6\text{O}_4\text{N}_4$ , thin, anisotropic platelets.

H. W.

**New Cases of Isomerism. II. Structural Association.** GUSTAV HELLER and WILLI KÖHLER (*Ber.*, 1923, 56, [B], 1595—1600).—It has been shown previously in three instances that an unexpected isomerism is observed in the case of *p*-lactams, as a consequence of which substances with the group  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{NH} \end{array}$  differ

from those containing the group  $C_6H_4\langle\begin{smallmatrix} C-OH \\ N \end{smallmatrix}\rangle$ . A similar instance is presented by *o*-hydrazinobenzoic anhydride,  $C_6H_4\langle\begin{smallmatrix} CO \\ NH \end{smallmatrix}\rangle NH$  (cf. Heller and Jacobsohn, A., 1921, i, 440), and 3-hydroxyindazole,  $C_6H_4\langle\begin{smallmatrix} C(OH) \\ N \end{smallmatrix}\rangle NH$  (cf. Thode, A., 1904, i, 347). The latter substance resembles the structurally similar isatole and 4-hydroxyquinoline in showing a more or less distinct tendency towards termolecular association in various solvents. To this tendency is attributed the ability of *p*-lactams to exist in two tautomeric forms, whereas in general only the lactam or the lactim is stable. It appears, therefore, that in these cases a new form of association is presented (structural association), as a consequence of which a form which is potentially tautomeric exists as a stable entity.

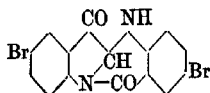
3-Hydroxyindazole (benzisopyrazolone), m. p. 206°, is conveniently obtained by heating *o*-aminobenzhydrazide at 200–210° in the presence of quinoline. It is converted by cautious treatment with acetic anhydride into 2-acetyl-3-hydroxyindazole,  $C_6H_4\langle\begin{smallmatrix} C(OH) \\ N \end{smallmatrix}\rangle NAc$ , m. p. 188° (decomp.), which is transformed when heated with glacial acetic acid into bis-*N*-acetylindazyl 3-ether,  $O(\langle\begin{smallmatrix} NAc \\ C_6H_4 \\ N \end{smallmatrix}\rangle)_2$ , m. p. 190°; the latter compound is hydrolysed by concentrated hydrochloric acid to monoacetylindazyl ether,  $C_{16}H_{12}O_2N_4$ , rhombic plates, m. p. 206°. 3-Hydroxyindazole is transformed by phosphoryl chloride and phosphorus pentachloride into bisbenzisopyrazolyl,  $C_6H_4\langle\begin{smallmatrix} CO \\ NH \end{smallmatrix}\rangle N-C\langle\begin{smallmatrix} C_6H_4 \\ NH \end{smallmatrix}\rangle N$ , leaflets, m. p. 228°, which is converted by acetic anhydride into a compound, needles, m. p. 250°. 3-Hydroxyindazole and nitrous acid yield 1:2-dinitroso-3-ketodihydroindazole,  $(C_6H_4\langle\begin{smallmatrix} CO \\ N(NO) \end{smallmatrix}\rangle)_2$ , pale yellow rhombohedra, m. p. 249° (decomp.). H. W.

**The Nature of Isatoids. II.** GUSTAV HELLER and HELLMUTH LAUTH (*Ber.*, 1923, 56, [B], 1591–1594).—Further examples of isatoids have been investigated.

5-Bromoisatin is treated with a solution of sodium in absolute alcohol. The precipitated sodium salt is removed and converted into the corresponding silver salt, which is treated with methyl iodide in the presence of ether and subsequently dissolved in acetic anhydride and exposed to light. 5-Bromo- $\beta$ -methylisatoid (5-bromoisatoid *O*-methyl ether),  $C_6H_3Br\langle\begin{smallmatrix} CO \\ NH \end{smallmatrix}\rangle C(OMe)\cdot N\langle\begin{smallmatrix} C_6H_3Br \\ CO \end{smallmatrix}\rangle CO$ , is thereby precipitated in orange-red needles, m. p. 262° (decomp.) after darkening at 225° and softening at 240°. When dissolved in hot benzene, it appears to become isomerised to the  $\alpha$ -form, m. p. 259–260° (decomp.) after incipient darkening at 238°. It is converted by *N*-sodium hydroxide solution into bromo- $\gamma$ -methylisatoid, m. p. 306–307° (decomp.) after becoming discoloured at about 190°, and more strongly so at 240–250°. 5-Bromoethyl-

isatoid crystallises in orange-red needles, m. p. 247° (decomp.) after darkening at 224° and softening at 240°; it does not appear to become isomerised in benzene solution. 5-Bromo-n-propylisatoid forms slender, orange-red needles, m. p. 232° (decomp.) after incipient decomposition at 227°.

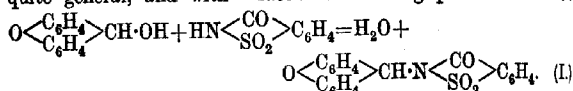
5-Bromomethylisatoid is converted by glacial acetic acid and hydrobromic acid (*d* 1.48) into anhydro-5-bromoindoxyl- $\alpha$ -4'-bromoanthranilide (annexed formula), small granules, m. p. 309–310° (decomp.); the compound is also obtained from 5-bromoethylisatoid. It is converted by chromic and glacial acetic acids into anhydro-5-bromoisatin- $\alpha$ -4'-bromoanthranilide, slender, yellow needles, m. p. 318°.



H. W.

**Indine and isoIndigotin.** O. DORNIER and JH. MARTINET (*Bull. Soc. chim.*, 1923, 33, 779–786).—A summary of the evidence on the subject of the composition of  $\alpha$ - and  $\beta$ -indines and of isoindigotin. The present authors conclude from spectrographic evidence that all three are identical. From the product of action of glycerol on dioxindole, they have isolated a violet powder which appears to be a mixture of indirubin and isoindigotin. H. H.

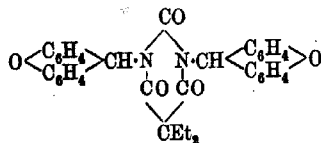
**Xanthyl Derivatives.** RENÉ FABRE (*Bull. Soc. chim.*, 1923, [iv], 33, 791–804).—Crystalline condensation products of xanthylol with substances containing a reactive hydrogen atom are described, and it is suggested that they may be of use for the characterisation of the parent substances. "Saccharin," antipyrine, and derivatives of veronal were studied in this connexion, the reaction being quite general, and with "saccharin" taking place as follows:



As a preliminary investigation, the  $p_H$  of some of the solutions employed was determined. Antipyrine, M/10 per litre,  $p_H=6.3$ ; pyramidone (dimethylaminoantipyrine), M/10 per litre,  $p_H=8.2$ ; veronal [5 : 5-diethylbarbituric acid], M/100 per litre,  $p_H=5.6$ ; "saccharin," M/1000 per litre,  $p_H=3.1$ .

The condensation is effected by means of acetic acid, which must be free from mineral acid. It is sufficient merely to warm a mixture of the acetic acid solutions of the components; on cooling, the condensed compound crystallises out and may be recrystallised

from the usual solvents. The following compounds are described: "xanthylsaccharin" (I), m. p. 199–200°; 1 : 3-dixanthyl-5 : 5-diethylbarbituric acid (annexed formula), m. p. 245–246°; 1 : 3-dixanthyl-5-phenyl-5-ethylbarbituric acid,



acid, m. p. 218–219°; 1 : 3-dixanthyl-5 : 5-diallylbarbituric acid,

m. p. 242—243°; 1:3-dioxanthyl-5-ethyl-5-butylbarbituric acid, m. p. 242—243°; 1:3-dioxanthyl-5-ethyl-5-isobutylbarbituric acid, m. p. 259—260°; 1-phenyl-4-xanthyl-2:3-dimethylpyrimidone, m. p. 178—179°. Pyrimidone, which contains no replaceable hydrogen atom, does not give a xanthyl derivative. H. H.

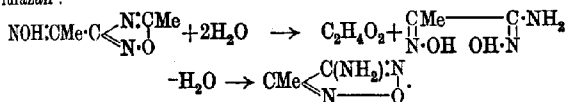
**Dioximes.** VII. G. PONZIO and G. RUGGERI (*Gazzetta*, 1923, 53, i, 297—305).—The relationship of aminomethylglyoxime (A., 1922, i, 627) to certain acyl derivatives of the azoximes and to aminomethylfuran has now been studied. The furazan derivative is not obtained directly from aminomethylglyoxime by elimination of a molecule of water from the two oximino-groups according to the usual method of preparing furazans from  $\alpha$ -dioximes. When, however, aminomethylglyoxime is boiled with excess of acetic anhydride, the following series of four reactions occurs: (1)  $\text{NOH}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOH} + \text{Ac}_2\text{O} \rightarrow \text{NOAc}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOAc}$ , (2)  $-\text{H}_2\text{O} \rightarrow \text{NOAc}:\text{CMe}:\text{C} \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{N}:\text{O} \end{smallmatrix}$ , (3)  $+\text{H}_2\text{O} \rightarrow \text{CH}_3:\text{CO}_2\text{H} +$

$\text{NOH}:\text{CMe}:\text{C} \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{N}:\text{O} \end{smallmatrix}$ ; the latter, on hydrolysis with dilute hydrochloric acid, (4)  $+\text{H}_2\text{O} \rightarrow \text{CH}_3:\text{CO}_2\text{H} + \text{CMe} \begin{smallmatrix} \text{C}(\text{NH}_2):\text{N} \\ \text{N}:\text{O} \end{smallmatrix}$ . The second

of these reactions is analogous to the synthesis of the azoximes from acyl derivatives of the amidoximes,  $\text{NH}_2:\text{CR}:\text{N}:\text{CO}:\text{OR}^1 \rightarrow$

$\text{H}_2\text{O} \rightarrow \text{CR} \begin{smallmatrix} \text{N}:\text{CR}^1 \\ \text{N}:\text{O} \end{smallmatrix}$ . The fourth reaction, representing the trans-

formation, not previously observed, of an azoxime into a furazan derivative, probably results first in the formation of an intermediate labile form of aminomethylglyoxime, which, unlike the stable form (*loc. cit.*), undergoes spontaneous anhydridation to aminomethylfuran:



This view is in agreement with the facts (1) that elimination of a molecule of water from the amino-group and the neighbouring benzoyl group of the dibenzoyl derivative of aminomethylglyoxime by treatment with boiling acetic anhydride yields the benzoyl derivative of the oxime of 3-acetyl-5-phenyl-1:2:4-oxadiazole,

$\text{OBz}:\text{N}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOBz} - \text{H}_2\text{O} = \text{OBz}:\text{N}:\text{CMe}:\text{C} \begin{smallmatrix} \text{N}:\text{CPh} \\ \text{N}:\text{O} \end{smallmatrix}$ ; (2) that,

from the same dibenzoyl derivative, by elimination of a molecule of water as above and replacement of a benzoyl group by a hydrogen atom by treatment with hot dilute sodium hydroxide solution, the oxime of 3-acetyl-5-phenyl-1:2:4-oxadiazole is obtained, and (3) that the last compound is convertible into aminomethylfuran by the action of dilute hydrochloric acid.

As regards aminomethylfuran, the presence of the amino-

group, modifies profoundly the properties of the ring,  $O \begin{smallmatrix} \diagup N:CM \\ \diagdown N:C \end{smallmatrix}$  which is not so stable as in the furazans,  $O \begin{smallmatrix} \diagup N:CR \\ \diagdown N:CR^1 \end{smallmatrix}$ , where R and

R<sup>1</sup> are alkyl or aryl groups. Aminomethylfuran may be diazotised by means of nitrous acid and then yields azoiminomethylfuran,  $N:CM \begin{smallmatrix} \diagup O-N \\ \diagdown C \end{smallmatrix} N:N \cdot NH \cdot C \begin{smallmatrix} \diagup CMe:N \\ \diagdown N-O \end{smallmatrix}$ , so readily that the diazo-

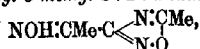
compound cannot be made to react with other bases. Moreover, although the methyl group of the methylfurazans is oxidisable to carboxyl, that of aminomethylfuran exhibits marked resistance towards energetic oxidising agents such as permanganate and concentrated nitric acid, which, however, dehydrogenate the amino-group, two residues then uniting to form azomethylfuran,  $N:CM \begin{smallmatrix} \diagup O-N \\ \diagdown C \end{smallmatrix} N:N \cdot C \begin{smallmatrix} \diagup CMe:N \\ \diagdown N-O \end{smallmatrix}$ ; the latter may be readily reduced to hydrazomethylfuran.

The *diacetyl* derivative of aminomethylglyoxime,



crystallises in lustrous prisms or flattened needles, m. p. 123° (anhydrous).

The *oxime* of 3-acetyl-5-methyl-1:2:4-oxadiazole,

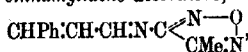


forms elongated prisms, m. p. 145°, and its *benzoyl* derivative,  $NOBz:CM \cdot C_3H_5ON_2$ , long needles, m. p. 198—199°.

The *oxime* of 3-acetyl-5-phenyl-1:2:4-oxadiazole,  $C_{10}H_9O_2N_3$ , crystallises in stout prisms, m. p. 205—209°, and its *benzoyl* derivative in long needles, m. p. 174—175°.

*Aminomethylfuran*,  $C_3H_5ON_3$ , crystallises in large, white, odourless prisms, m. p. 72—73°, does not volatilise in a current of steam, and remains unchanged when heated with sodium hydroxide solution or hydrochloric acid. Its *acetyl* derivative,  $C_3H_5ON_2NHAc$ , crystallises in lustrous laminae, m. p. 115—116°; its *benzylidene* derivative,  $CHPh(NH \cdot C \begin{smallmatrix} \diagup N-O \\ \diagdown CMe:N \end{smallmatrix})_2$ , in flattened needles, m. p.

155—156°, and its *cinnamylidene* derivative,



forms straw-coloured laminae, m. p. 126°.

*Azomethylfuran*,  $C_6H_6O_2N_4$ , forms orange laminae, m. p. 107°, and *hydrazomethylfuran*,  $C_6H_6O_2N_4$ , which is readily oxidised to the azo-compound, white prisms (+H<sub>2</sub>O), m. p. 118—119° (slight decomp.).

*Azoiminomethylfuran*,  $C_6H_6O_2N_7$ , crystallises in straw-coloured laminae (+aq.), m. p. 114°; its *silver* salt,  $C_6H_6O_2N_7Ag$ , forms a white powder stable towards light and explodes violently when heated; its *acetyl* derivative,  $C_6H_6O_2N_7$ , crystallises in white laminae, m. p. 72°.

T. H. P.

**Dioximes. VIII.** G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, 53, i, 305—311).—By the action of aniline on the peroxide of  $\alpha$ -phenylglyoxime (phenylfuroxan) in benzene solution, Wieland and Semper (A., 1908, i, 108) obtained a compound, m. p. about 180° (decomp.), which, from its method of formation and from the intense colour it gives with ferric chloride, they regarded as the substituted amidoxime,  $\text{NOH}\cdot\text{CPh}\cdot\text{C}(\text{NOH})\cdot\text{NHPh}$ . The authors find that this anilinophenylglyoxime exists in two modifications interrelated in the same way as the two aminophenylglyoximes (this vol., i, 472).  $\alpha$ -Anilinophenylglyoxime, m. p. 188°, when prepared as described by Wieland and Semper, is accompanied by another compound, m. p. 202°, which is being investigated. This  $\alpha$ -compound does not form complex salts, but the  $\beta$ -isomeride, obtained either by the action of dilute acetic acid on the  $\alpha$ -form or by the interaction of aniline and chlorophenylglyoxime (this vol., i, 473), acts in aqueous solution on certain metals of the eighth group with formation of the corresponding complex salts. Both  $\alpha$ - and  $\beta$ -forms exhibit distinct basicity and yield moderately stable hydrochlorides, but are also soluble in strong bases.

The action of aniline on chloromethylglyoxime or that of hydroxylamine on acetylphenylisouretin yields  $\beta$ -anilinoethylglyoxime, which is a strong base but unstable, and gives a complex nickel compound.

$\alpha$ -Anilinophenylglyoxime forms : a *hydrochloride*,  $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3\cdot\text{HCl}$ , long, white needles, m. p. 208—209° (decomp.), which is moderately stable in the air but is rapidly hydrolysed by water; a *diacetyl* compound,  $\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_3$ , white needles, m. p. 179°, which yields  $\alpha$ -anilinophenylglyoxime, together with a little phenylaminophenylfuran (see below), when suspended in 20% sodium hydroxide solution; a *dibenzoyl* compound,  $\text{C}_{28}\text{H}_{21}\text{O}_4\text{N}_3$ , which forms small crystals, m. p. 201°, and is not appreciably changed when heated with 20% sodium hydroxide solution.

*Anilinophenylfuran*,  $\text{O} < \begin{smallmatrix} \text{N}:\text{CPh} \\ \text{N}:\text{C}\cdot\text{NHPh} \end{smallmatrix}$ , obtained by boiling  $\alpha$ -anilinophenylglyoxime with 20% sodium hydroxide solution (see above), forms lustrous, white needles, m. p. 158°.

$\beta$ -Anilinophenylglyoxime,  $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3$ , crystallises in small, white needles, m. p. 124° (slight decomp.) with previous softening, gives an intense blue coloration with ferric chloride, and, in aqueous solution, attacks compact nickel even in the cold and copper and cobalt when heated. The *hydrochloride*,  $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3\cdot\text{HCl}$ , forms rhombic plates, m. p. 210—211° (decomp.); the *nickel* salt,  $(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3)_2\text{Ni}$ , dark red prisms or thin, pale coffee-coloured, silky laminae (+2H<sub>2</sub>O), m. p. 268° (decomp.), not reacting with ammonia solution; and the *diacetyl* derivative,  $\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_3$ , groups of white needles, m. p. 150°, with previous softening.

*Anilinoethylglyoxime*,  $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NOH})\cdot\text{NHPh}$ , is unstable; its *nickel* salt,  $(\text{C}_9\text{H}_{10}\text{O}_2\text{N}_3)_2\text{Ni}$ , crystallises in lustrous, wine-red laminae, m. p. 242° (decomp.), and dissolves in 20% sodium hydroxide solution giving a brownish-red coloration, but is insoluble in ammonia solution.

T. H. P.

**Dioximes.** IX. G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, 53, i, 311—318).—Further experimental data are described which show the marked difference in behaviour between the two forms of phenylglyoxime and thus confirm the view that the isomerism of the  $\alpha$ -dioximes cannot be explained by the theory of Hantzsch and Werner.

When treated with concentrated sulphuric acid,  $\alpha$ -phenylglyoxime loses a molecule of water, giving phenylfurazan, whereas two molecules of the  $\beta$ -isomeride lose a molecule of hydroxylamine with formation of the compound,  $C_{16}H_{13}O_3N_3$ , already obtained by Müller and Pechmann (A., 1890, 51) by treating phenylglyoxal with hydroxylamine hydrochloride, by Scholl (A., 1891, 287) by heating oximinooacetophenone with excess of hydroxylamine hydrochloride, by Korten and Scholl (A., 1901, i, 549) by the action of hydroxylamine on  $\omega$ -dibromoacetophenone, and by Diels and Sasse (A., 1907, i, 1086) by preparing the oxime of the product resulting from the anhydridation of oximinooacetophenone. The method used by the authors to obtain this compound is in agreement with Scholl and Baumann's view that it consists of 1-phenyl-3-oximinobenzyl-2-isooxazolonoxime (A., 1907, i, 492).

Both dioximes of phenylglyoxal are readily coupled with phenyl diazonium chloride yielding unstable compounds which readily lose nitrogen and then give  $\alpha$ - and  $\beta$ -benzildioximes, respectively; the latter only forms a complex nickel compound. Just as with the phenylglyoximes, these two benzildioximes cannot be regarded as geometrical isomerides.

The authors confirm Russanov's statement (A., 1892, 321) that both forms of phenylglyoxime yield the same diacetyl derivative, and find that the  $\alpha$ - but not the  $\beta$ -compound yields at the same time phenylfurazan, and that the  $\alpha$ -compound cannot be benzoylated. The conclusion is drawn that  $\alpha$ -phenylglyoxime yields a diacetyl derivative, not directly, but only after isomerisation to the  $\beta$ -form. This view is confirmed by the fact that the action on the two phenylglyoximes of propionic anhydride, which exhibits comparatively slight dehydrating properties, yields two different dipropionyl derivatives.

*Dipropionyl- $\alpha$ -phenylglyoxime*,  $COEt \cdot ON : CPh \cdot CH : NO \cdot COEt$ , crystallises in prisms, m. p.  $75^\circ$ , and is slowly dissolved by 20% sodium hydroxide solution, with formation of phenylfurazan, which then undergoes partial isomerisation into benzoyl cyanide oxime (oximinobenzyl cyanide) under the influence of the strong base.

*Dipropionyl- $\beta$ -phenylglyoxime* crystallises in laminae, m. p.  $89$ – $90^\circ$ , and is converted into  $\beta$ -phenylglyoxime by treatment with 20% sodium hydroxide solution.

*Dibenzoyl- $\beta$ -phenylglyoxime*,  $C_{22}H_{16}O_4N_2$ , forms flattened needles, m. p.  $150^\circ$ .

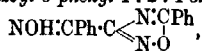
Attempts to benzoylate  $\alpha$ -phenylglyoxime in pyridine solution results in the formation of the benzoyl-derivative of benzoyl cyanide oxime (Zimmermann, A., 1903, i, 91).

Phenylfurazan crystallises in white prisms, m. p.  $35$ – $36^\circ$  (cf. Russanov, *loc. cit.*).  
T. H. P.

**Dioximes.** X. G. PONZIO and L. AVOGADEO (*Gazzetta*, 1923, 53, i, 318—327; cf. this vol., i, 472).—Treatment of  $\alpha$ -aminophenylglyoxime with acetic anhydride in the cold yields the diacetyl derivative,  $\text{NOAc}:\text{CPh}:\text{C}(\text{NHAc})\text{:NOH}$ , which is converted by sodium hydroxide into acetamidophenylfurazan. Under similar conditions,  $\beta$ -aminophenylglyoxime gives the diacetyl compound,  $\text{NOAc}:\text{CPh}:\text{C}(\text{NH}_2)\text{:NOAc}$ , which, with sodium hydroxide, yields first 3-acetoximinobenzyl-5-methyl-1:2:4-oxadiazole and then 3-oximinobenzyl-5-methyl-1:2:4-oxadiazole. When either the latter or acetamidophenylfurazan is heated with dilute hydrochloric acid, aminophenylfurazan is obtained. From these results it is evident that the two oximino-groups of  $\beta$ -aminophenylglyoxime are equivalent, whereas those of the  $\alpha$ -isomeride are not equivalent. The action of sodium hydroxide on the dibenzoyl derivative of  $\alpha$ -aminophenylglyoxime yields aminophenylfurazan and 3-oximinobenzyl-5-phenyl-1:2:4-oxadiazole, whereas the dibenzoyl compound of the  $\beta$ -glyoxime gives the latter itself and also 3-oximinobenzyl-5-phenyl-1:2:4-oxadiazole, which is converted into aminomethylfurazan by means of dilute hydrochloric acid. The action of water on the oximes of 3-acyl-5-alkyl(or aryl)-1:2:4-oxadiazoles serves as a general method for the preparation of aminofurazans. The behaviour of such oximes is, indeed, entirely different from that of the isomeric 3-acyl-5-aminoaryl-1:2:4-oxadiazoles, investigated by Holleman (A., 1893, i, 205), Böseken (A., 1898, i, 696; 1910, i, 643) and Wieland and Gmelin (A., 1910, i, 784). Thus, the oxime of 3-benzoyl-5-phenyl-1:2:4-oxadiazole yields benzoic acid and aminophenylfurazan when heated with dilute hydrochloric acid, whereas 3-benzoyl-5-anilino-1:2:4-oxadiazole gives benzoic acid and phenylcyanocarbamide when heated with sodium hydroxide.

*Diacetyl- $\alpha$ -aminophenylglyoxime*,  $\text{NOAc}:\text{CPh}:\text{C}(\text{NHAc})\text{:NOH}$ , crystallises in flattened needles, m. p. 150—151°, and the dibenzoyl compound in slender needles, m. p. 189—190° (Wieland and Semper, A., 1908, i, 108, gave m. p. 176°).

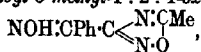
The oxime of 3-benzoyl-5-phenyl-1:2:4-oxadiazole,



forms slender needles, m. p. 148°.

*Diacetyl- $\beta$ -aminophenylglyoxime*,  $\text{NOAc}:\text{CPh}:\text{C}(\text{NH}_2)\text{:NOAc}$ , crystallises in large prisms, m. p. 133—134°.

The oxime of 3-benzoyl-5-methyl-1:2:4-oxadiazole,



forms lustrous, white needles, m. p. 202—203° (slight decomp.), its acetyl derivative,  $\text{NOAc}:\text{CPh}:\text{C}(\text{ON}_2\text{Me})\text{:NOAc}$ , needles, m. p. 101—102°, and its benzoyl derivative,  $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}_3$ , long, slender needles, m. p. 152—153°.

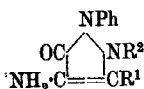
*Dibenzoyl- $\beta$ -aminophenylglyoxime*,  $\text{NOBz}:\text{CPh}:\text{C}(\text{NH}_2)\text{:NOBz}$ , crystallises in flattened prisms, m. p. 185—186°.

*Aminophenylfurazan*,  $\text{O} \begin{array}{l} \nearrow \text{N}:\text{CPh} \\ \searrow \text{N}:\text{C}:\text{NH}_2 \end{array}$ , crystallises in white prisms

or long needles, m. p. 98—99°, and is stable towards alkali hydroxide, concentrated hydrochloric or sulphuric acid or 4*N*-nitric acid, even when heated, but decomposes violently with formation of *p*-nitrobenzoic acid when heated with concentrated nitric acid (*d* 1.4). Its acetyl derivative,  $C_6ON_2Ph \cdot NHAc$ , crystallises in lustrous needles, m. p. 181—182°, and its diacetyl derivative,  $C_6ON_2Ph \cdot NAc_2$ , in long, broad laminae, m. p. 71°.

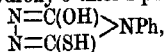
Azophenylyfurazan,  $C_6ON_2Ph \cdot N \cdot N \cdot C_6ON_2Ph$ , forms long, orange needles, m. p. 134—135°, and hydrazophenylyfurazan,  $C_{12}H_{10}O_2N_6$ , almost white laminae, m. p. 169°.

**Preparation of Carbamic Acid Derivatives of the Pyrazolone Series.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360424; from *Chem. Zentr.*, 1923, ii, 407—408).—4-Amino-pyrazolones or their derivatives are treated with alkali hydrogen carbonates. Basic pyrazolones of the accompanying general formula (where  $R_1$  and  $R_2$  = hydrogen or alkyl), and in which the phenyl group may or may not be substituted, are thereby changed into soluble alkali salts with neutral reaction. An alkali carbonate, or hydroxide in the presence of carbon dioxide, may be used in place of a hydrogen carbonate. 4-Amino-1-phenyl-2:3-dimethyl-5-pyrazolone gives a corresponding carbamate; it is a white powder. 1-*p*-Arsenodiphenyl-di(4-amino-5-pyrazolone) (A., 1921, i, 752) gives a carbamate as a clear, stable solution.



**Preparation of 4-Dimethylamino-1-aryl-2:3-dialkyl-5-pyrazolones.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360423; from *Chem. Zentr.*, 1923, ii, 407).—4-Amino-1-aryl-2:3-dialkyl-5-pyrazolones are treated with formaldehyde or its polymerisation products in the presence of aqueous formic acid. Methylation takes place without formation of quaternary ammonium bases. 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone, 4-dimethylamino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone, m. p. 107°, and 4-dimethylamino-1-*p*-tolyl-2:3-dimethyl-5-pyrazolone, m. p. 105°, are mentioned.

**Syntheses of 3-Hydroxy-5-thioltriazoles.** E. FROMM and E. NEHRING (*Ber.*, 1923, 56, [B], 1370—1375).—Ethyl 8-phenylthiosemicarbazide- $\alpha$ -carboxylate,  $NHPh \cdot CS \cdot NH \cdot NH \cdot CO_2Et$ , slender crystals, m. p. 141°, is prepared by the gradual addition of ethyl chloroformate to a boiling alcoholic suspension of 8-phenylthiosemicarbazide; it is converted by boiling, aqueous sodium hydroxide solution into 3-hydroxy-5-thiol-4-phenyltriazole,



coarse prisms (+ $H_2O$ ), m. p. 193° after softening at 130—140°. The lead salt,  $C_{16}H_{12}O_2N_6S_2Pb$ , is described. 3-Hydroxy-5-benzylthiol-4-phenyltriazole crystallises in colourless needles, m. p. 158°; it is converted by benzoyl chloride into 3-hydroxy-2-benzoyl-5-benzylthiol-4-phenyltriazole, colourless needles, m. p. 122°. 3-Hydroxy-

*3-hydroxy-5-benzylthio-4-phenylmethyldiazole* has m. p. 126°. 3-Hydroxy-5-thiol-4-phenyltriazole combines with phenylhydrazine to form the salt,  $C_{14}H_{15}ON_3S$ , colourless crystals, m. p. 169°; it is oxidised by bromine water to the corresponding disulphide,  $C_{16}H_{17}O_2N_3S_2$ , m. p. 286°.

The action of ethyl chloroformate on thiosemicarbazide in the presence of benzene leads to the formation of mixtures which are almost non-separable into their components; on one occasion, *ethyl semicarbazidedicarboxylate* (?), m. p. 130°, was isolated. In alcoholic solution, on the other hand, the substances yield *ethyl thiosemicarbazide- $\alpha$ -carboxylate*,  $NH_2\cdot CS\cdot NH\cdot NH\cdot CO_2Et$ , colourless crystals, m. p. 184°, in which the position of the carbethoxyl group is proved by the failure of the compound to react with benzaldehyde. It is converted by benzyl chloride and sodium hydroxide in the presence of alcohol into ethyl 8-benzylisothiosemicarbazide-carboxylate,  $CH_2Ph\cdot S\cdot C(NH)\cdot NH\cdot NH\cdot CO_2Et$ , m. p. 145°. It is transformed by two equivalent proportions of sodium hydroxide in aqueous solution into 3-hydroxy-5-thioltriazole, m. p. 202° (Arndt, A., 1922, i, 277 gives m. p. 206°), which is most readily prepared by the action of hydrogen sulphide on the corresponding lead salt. 3-Hydroxy-5-benzylthioltriazole crystallises in colourless leaflets, m. p. 182°; the corresponding *diacetyl* compound forms colourless needles, m. p. 89°. 3-Hydroxy-5-thioltriazole gives a salt with phenylhydrazine, m. p. 155°; it is converted by bromine water into the disulphide,  $C_4H_4O_2N_3S_2$ , m. p. 245°. H. W.

**The leuco-Sulphinic Acids of the Triphenylmethane Dyes.** G. SCHEUING and R. BERLINER (*Ber.*, 1923, 56, [B] 1583—1568; cf. Wieland, A., 1919, i, 355; Wieland and Scheuing, A., 1922, i, 58).—Under suitable conditions, paramagenta can be dissolved in alkaline sodium hyposulphite solution to yield a concentrated vat from which *ammonium paramagentaleucosulphinate*,



is precipitated by addition of solid ammonium chloride and *paramagentaleucosulphinic acid*,  $C_{19}H_{19}O_2N_3S_2H_2O$ , is obtained by cautious addition of acetic acid. They are soluble in cold, dilute alkali hydroxide, but decompose rapidly in warm solution into *para*leucoaniline and sulphite. The neutral solution of the sodium salt is oxidised by air with production of the paramagenta salt of paramagentaleucosulphonic acid; in the presence of an excess of alkali hydroxide the products are leucoaniline, and a mixture of rosaniline and the salt of the leucosulphonic acid. In acid solution, the leucosulphonic acid undergoes autoxidation to paramagenta and sulphurous acid.

The direct conversion of paramagentaleucosulphinic acid into the corresponding sulphinic acid does not appear to be capable of accomplishment.

In a similar manner, aurin is converted into *sodium aurinleucosulphinate*,  $C_{19}H_{19}O_2SNa$ , which is less stable than the similar compounds which have been described previously. In other respects it resembles these substances very closely. Autoxidation

of the sulphinic acid in alkaline solution leads to the production of sulphite and aurin; the latter is mixed with 4:4'-dihydroxybenzophenone, so that a benzene nucleus is removed from the dye by the action of atmospheric oxygen.

H. W.

**The Bromine Reaction of Magenta-sulphurous Acid.** G. SCHEUTING and O. SCHAAFF (*Ber.*, 1923, 56, [B], 1588—1591).—Guareschi (A., 1913, ii, 333) has shown that magenta-sulphurous acid can be used for the detection of bromine, with which it gives a reddish-violet coloration, whereas chlorine gives a pale yellow coloration and iodine is without action; confusion with the aldehyde reaction is avoided by the use of solutions which do not contain free sulphurous acid.

The action of an excess of cold bromine water on a solution of paramagenta-leucosulphonic acid in dilute hydrochloric acid leads to the production of hexabromoparasosanine, which, in part, undergoes further oxidation to tetrabromo-4:4'-diamino benzophenone. Paramagenta itself behaves in a similar manner. In both cases, bromination appears to proceed directly to the formation of the hexabromo-derivative. In the case of the sulphonic acid, the loss of sulphur dioxide occurs spontaneously from the hexabrominated derivative:  $\text{HCl}(\text{H}_2\text{N}\cdot\text{C}_6\text{H}_2\text{Br}_2)_3\cdot\text{C}\cdot\text{SO}_3\text{H} = (\text{H}_2\text{N}\cdot\text{C}_6\text{H}_2\text{Br}_2)_2\cdot\text{C}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{NH}\cdot\text{HCl} + \text{H}\cdot\text{SO}_3\text{H}$ .

The bromine reaction of Schiff's reagent thus resembles closely the reaction with aldehydes. In both cases, a leucosulphonic acid is formed which decomposes spontaneously into dye and sulphurous acid. A difference is found in the ability of bromine to produce the unstable-sulphonic acid immediately, whereas with aldehyde a more stable, partly substituted sulphonic acid is formed as intermediate product.

H. W.

**Xanthyl Derivatives of Allophanic Acid, Thiosinamin and Allantoin.** R. FOSSE and A. HIEULLE (*Compt. rend.*, 1922, 176, 1719—1721).—The allophanic esters in diluted acetic acid solution condense with xanthidrol to give a xanthyl derivative, m. p. 230°, having the constitution  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH} < \text{C}_6\text{H}_4 >$ .

Like the mono-substituted thiocarbamides, thiosinamine also condenses with xanthidrol, giving a monoxanthyl derivative, which decomposes on heating at 159—165°. Similarly, allantoin gives xanthyllallantoin,  $\text{O} < \text{C}_6\text{H}_4 > \text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH} < \text{NH}\cdot\text{CO} > \text{CO}\cdot\text{NH}$ , which

crystallises in characteristic tabular crystals, m. p. 214—215. The above xanthyl derivatives are valuable for the detection and characterisation of the parent substances in biochemical work, an allantoin, for example, was easily identified by means of its xanthyl derivative in the urine of the dog and rabbit, and in the young leaves of the plane tree.

G. F. M.

**The Influence of Hydrogen-ion Concentration on the Solubility of Uric Acid. II.** A. JUNG (*Helv. Chim. Acta*, 1923, 6, 562—593).—In a previous paper (A., 1922, i, 1070)

as shown that the solubility of uric acid is influenced by the hydrogen-ion concentration, and it is now shown that the results obtained fit in with Michaelis's formula,  $\Lambda = \lambda + k\lambda/[H^+]$ , where  $\Lambda$  is the total solubility,  $\lambda$  is the partial solubility (the solubility when dissociation is suppressed), and  $k$  is the dissociation constant. Although the ammonium salt is the least soluble salt of uric acid, ammonium compounds in the buffer solution do not influence the solubility of uric acid provided  $p_H$  is less than 6.8. The solubility of other urates in water corresponds with the hydrogen-ion concentration brought about by the hydrolysis of the salt. A large number of solubility measurements were made at 18° and at 37°, using uric acid and sodium urate in different buffer salt solutions, and it is concluded that the results obtained can generally be interpreted by the mass action law. Uric acid and a urate can exist in solution side by side, but the solubility product of the least soluble urate is never exceeded. The variable results obtained sometimes in urate and uric acid solubility determinations may be accounted for by the slow rate at which equilibrium may be attained between the dissociated and undissociated acid and its salts. Dissociated uric acid and its salts change gradually in salt solutions into the sparingly soluble undissociated acid, and the slowness of this change may lead to apparently irreconcilable results. Sodium urate readily undergoes bacterial decomposition, which is specially rapid in pure water and in sodium phosphate solutions.

E. H. R.

**Diazotisation of *p*-Nitroaniline.** CHARLES SUNDER and HENRI SUNDER (*Bull. Soc. Ind. Mulhouse*, 1923, 89, 237—240).—The diazotisation of *p*-nitroaniline is most conveniently carried out by quickly adding dilute hydrochloric acid (an excess not greater than one-tenth molecule is used) to a solution containing the theoretical amounts of sodium nitrite and *p*-nitroaniline at 10—14°. An unsatisfactory result is obtained when the addition is made in the reverse order. If the diazotisation of *p*-nitroaniline is effected in the presence of an excess of hydrochloric acid not exceeding one-tenth molecule, the solution thereby obtained may be used for the production of good shades of Para-red without adding sufficient sodium acetate to convert the whole of the diazonium chloride into the corresponding acetate. [Cf. *J.S.C.I.*, 1923, 713A.]

A. J. H.

**The Diazonium Hydroxides of Anthraquinone.** M. BATTAY and J. BÉHA (*Bull. Soc. Ind. Mulhouse*, 1923, 89, 241—246).—By diazotisation of  $\alpha$ - and  $\beta$ -aminoanthraquinones and preparation of the corresponding chloroplatinates, chloraurates, and cobaltinitrites, it is shown that anthraquinonediazonium hydroxide exists in the form  $C_{14}H_7O_2-N-OH$ .



A solution of anthraquinonediazonium

hydroxide was obtained by the careful addition of barium hydroxide to a solution containing anthraquinonediazonium hydrogen sulphate and subsequently removing, by filtration, the barium sulphate

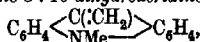
thereby precipitated. In solution, when freshly prepared at 0°, was alkaline to methyl-orange, Thiazole Yellow, and Dobbin's reagent, but it became acidic within a few minutes (the  $\alpha$ -diazonium compound was more stable than the  $\beta$ -compound) owing to formation of the corresponding antidiazo-compounds,  $C_{14}H_7O_2N$ .

Crystalline compounds were obtained by addition of chloroplatinic acid, chloroauric acid, and sodium cobaltinitrite to solutions containing anthraquinonediazonium hydroxide, a good yield of the chloroplatinate of diazo- $\alpha$ -anthraquinone being thereby quite readily obtained, since it is only slightly soluble in water or dilute alcohol. When sodium chloroplatinate is used instead of chloroplatinic acid, formation of the chloroplatinate of diazoanthraquinone is not complete, since the sodium hydroxide formed in the reaction, converts a portion of the diazonium hydroxide into the antidiazoate which does not form a chloroplatinate.

A. J. H.

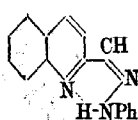
**The Mechanism of Coupling Reactions. III. The Production of Azo-dyes from 1-Alkyl-2-methylenedihydroquinolines.** W. KÖNIG (*Ber.*, 1923, 56, [B], 1543—1550).—1-Alkyl-2-methylenedihydroquinolines couple readily with diazo-compounds; the alkyl groups are thereby replaced by hydrogen and a class of iminoazo-dyes is produced. Such dyes which contain the nitro-group in the para-position in the diazonium component yield normal yellow hydrochlorides, whereas the corresponding free bases appear to belong to a class of inner hydrogen complex salts which in their colour resemble the alkali conjunction-salts of the *p*-nitrophenylhydrazones of quinoline-2-aldehyde. The azo-dyes and the hydrazones of this class are geometrical isomerides, the former having the *syn*- and the latter the *anti*-configuration.

10-Methyl-5-methylene-5:10-dihydroacridine,



pale yellow needles, m. p. 93°, is prepared by the action of sodium hydroxide in the presence of ether on an aqueous solution of 5:10-dimethylacridinium perchlorate. In the acridine series, the isolation of the methylene base in substances is thus shown to be possible, whereas this does not appear to be the case in the quinoline series.

2-Benzeneazomethylene-1:2-dihydroquinoline (annexed formula)



is obtained in the form of its *hydrochloride*, reddish-yellow needles, m. p. 211—212°, by the simultaneous addition of solutions of sodium hydroxide and phenyldiazonium chloride to 2-methylquinoline methiodide dissolved in water; the free base could not be caused to crystallise. 2-*p'*-Nitrobenzene-

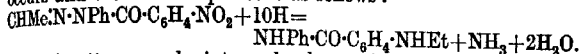
azomethylene-1:2-dihydroquinoline *hydrochloride*, dark red needles, m. p. 241°, is prepared in a similar manner from 2-methylquinoline methiodide, ethiodide, or isoamylidide; the corresponding free base crystallises in small, almost black needles with a bronze reflex, m. p.

171°. The anti-*p*-nitrophenylhydrazones of quinoline-2-aldehyde, yellowish-brown needles, m. p. 245°, is prepared from its components in boiling alcoholic solution; the corresponding sodium salt, the hydrochloride, tile-red needles, m. p. 258°, and the sulphate are described.

H. W.

The Action of Halogens on Phenylhydrazones. I. The Action of Bromine. JAMES ERNEST HUMPHRIES, EDWARD BLOOM, and ROY EVANS (T., 1923, 123, 1766—1772).

Migration of Alkyl and Alkaryl Residues in the Reduction of Nitrobenzoylphenylhydrazones. GEORG LOCKEMANN (Z. angew. Chem., 1923, 36, 349—351).—The action of *p*-nitrobenzoyl chloride on phenyl- $\alpha$ -ethylidenhydrazine [acetaldehydephenylhydrazone] in the presence of pyridine and complete absence of moisture yields a *p*-nitrobenzoylphenylethylidenhydrazine melting at 116—116.5° (cf. Lockemann and Liesche, A., 1906, 1, 111). This, when reduced with zinc dust and sulphuric acid, does not give rise to *p*-aminobenzanilide and ethylamine, but migration occurs and the reaction proceeds as follows:



This migration may be intramolecular, or intermolecular with the intermediate formation of a Schiff's base.  $\alpha$ -*p*-Nitrobenzoyl-*p*-tolyl- $\beta$ -ethylidenhydrazine (m. p. 149—150°) and the *p*-nitrobenzoyl derivative of phenylpropylidenhydrazine behave just like the above when reduced with zinc and sulphuric acid. In the case of the *p*-nitrobenzoylphenylbenzylidenhydrazines the acid used largely determines the course of the reaction. With zinc and sulphuric acid the *p*-compound yields mainly, and the *o*- and *m*-compounds only, aminobenzanilide and benzylamine, whilst, if acetic acid is used instead of sulphuric, a considerable proportion of benzylaminobenzanilide is formed, the reaction proceeding in the latter sense to the extent of 42% with the ortho-compound, 35% with the meta-compound, and 60% with the para-compound.

W. T. K. B.

#### Enantiotropic Transformation of Phthalylphenylhydrazide.

FUSAO ISHIKAWA (Bull. Inst. Phys. Chem. Res. [Rikugaku Kenkyu Jo Ikk], 1923, 2, 264—267).—Chattaway and Lambert (T., 1915, 107, 1773) determined the solubility of phthalylphenylhydrazide in chloroform, ethyl acetate, and acetone and found its transition point to be 9.5°. From the solubility data, the author has calculated the heat of transition, the transition point, and the transition affinity of the compound. The heat of transition of 1 g. of the light yellow modification into the deep yellow one at 9.5° in chloroform is 2.72 cal. and in ethyl acetate 2.89 cal. From the solubility in chloroform at 5° and 15°, the transition point was calculated to be 9.4°. From the solubility in chloroform, the transition affinity per 1 g. molecule was calculated as follows: For the change  $\beta \rightarrow \alpha$ , 5.75 cal. at 5°, 2.38 cal. at 8°, and 1.26 cal. at 9°. For the change  $\alpha \rightarrow \beta$ , 1.78 cal. at 10°, 2.28 cal. at 11°, 7.41 cal. at 15°, and 21.49 cal. at 25°.

From the solubilities at 25°, the transition affinities in chloroform,

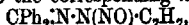
ethyl acetate, and acetone per 1 g. molecule are 21.40, 21.35, and 21.98 cal. respectively.

K. K.

**Nitrosohydrazones.** II. M. BUSCH and S. SCHÄFFNER (*Ber.*, 1923, 56, [B], 1612—1616).—It has been shown previously that the nitroso-derivatives of aldehydrazones are nitrosoamines, and that their conversion into nitroaldehydrazones is due to the migration of the nitroso-group from nitrogen to carbon. In nitrosoketohydrazones, the nitroso-group shows a similar tendency to change its place in the molecule, so that, by union with another atom of oxygen, nuclear nitration ensues. In this manner, nitrosobenzophenonephenylhydrazone,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NPh}\cdot\text{NO}$ , yields benzophenone-*p*-nitrophenylhydrazone,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . The properties of the latter substance are very similar to those of the compound obtained by Bamberger, Schmidt, and Levinstein (*A.*, 1900, 1, 566) from diazotised aniline and nitromethane in alkaline solution, and considered by them to be benzeneazoneitrodiphenylmethane,  $\text{NO}_2\cdot\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NPh}$ . Re-examination of the reaction has shown that the ultimate product is benzophenone-*p*-nitrophenylhydrazone, which results from the isomerisation of primarily formed benzeneazoneitrodiphenylmethane by boiling alcohol used in its purification.

A series of further examples of the conversion of nitrosoketohydrazones into nuclear nitrated hydrazones is given.

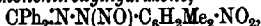
**Benzophenone-*p*-tolylhydrazone**, pale yellow leaflets or large plates, m. p.  $88^\circ$ , is converted by sodium nitrite in the presence of glacial acetic acid into the corresponding *nitrosoamine*,



lemon-yellow needles, m. p.  $108^\circ$  after darkening at  $98^\circ$  and softening with evolution of nitrous fumes above  $100^\circ$ . When dissolved in ether containing a little acetic acid, the nitrosoamine gradually passes at the atmospheric temperature into **benzophenone-*o*-nitro-*p*-tolylhydrazone**,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NH}\cdot\text{C}_7\text{H}_7\cdot\text{NO}_2$ , pale red, transparent leaflets, m. p.  $164^\circ$ . The nitro-compound is reduced by zinc dust and acetic acid to **benzophenone-*o*-amino-*p*-tolylhydrazone**, yellow leaflets, m. p.  $202^\circ$ .

**Benzophenone-*o*-tolylhydrazone**, pale yellow, cubic crystals, m. p.  $102^\circ$ , is converted by sodium nitrite and glacial acetic acid into **benzophenone-*p*-nitro-*o*-tolylhydrazone**, straw-yellow, prismatic rods, m. p.  $176^\circ$ .

**Benzophenone-*as*-*m*-xyllylhydrazone**, pale yellow, lustrous needles, m. p.  $84^\circ$ , is transformed by nitrous acid into the *nitrosoamine*,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{N}(\text{NO})\cdot\text{C}_8\text{H}_9$ , lustrous, orange-yellow prisms, m. p.  $104^\circ$  (a diazonium salt is simultaneously produced by fission of the hydrazone). When dissolved in benzene and treated with alcoholic hydrogen chloride, the nitrosoamine is converted into the *nitrosoamine* of **benzophenonenitroxylhydrazone**,



lustrous, blood-red needles, m. p.  $119$ — $120^\circ$  (decomp.). H. W.

**Tetrazones from Hydrazones and Azo-compounds.** M. BUSCH, HELMUT MÜLLER, and EUGEN SCHWARZ (*Ber.*, 1923, 56, [B], 1600—1612).—It has been shown previously that benzal-

hydephenylhydrazone unites readily with benzeneazobenzoyl to give an unstable tetrazen derivative which readily passes into the stable hydrazinohydrazone or becomes converted into the formazyl derivative (cf. Busch and Kunder, A., 1917, i, 56). Similar observations are now recorded with a series of similar azo-compounds.

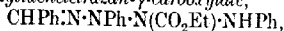
The action of azodibenzoyl on benzaldehydephenylhydrazone in ethereal solution leads to the production of  $\gamma\delta$ -dibenzoyl- $\beta$ -phenyl- $\alpha$ -benzylidenetetrazen,  $\text{CHPh:N:NPh:Nbz:NHBz}$ , yellow needles, m. p. 139°. It is readily reduced to benzaldehydephenylhydrazone and dibenzoylhydrazine. When heated slightly above its melting point or when treated with boiling alcohol containing a little hydrochloric acid, it becomes isomerised to dibenzoylhydrazinobenzaldehydephenylhydrazone,  $\text{NHPh:N:CPh:Nbz:NHBz}$ , colourless needles, m. p. 192°; the constitution of the substance is deduced from its hydrolysis to tribenzoylhydrazine and phenylhydrazine. The tetrazen is not affected by ammonia or pyridine.

The interaction of azodibenzoyl with benzaldehyde-*p*-bromophenylhydrazone in cold ethereal solution gives rise to dibenzoylhydrazinobenzaldehyde-*p*-bromophenylhydrazone, colourless, crystalline needles, m. p. 200°, as isolatable product; it is hydrolysed to tribenzoylhydrazine and *p*-bromophenylhydrazine.

Azodibenzoyl reacts with the  $\beta$ - and  $\alpha$ -forms of acetaldehydephenylhydrazone to give  $\beta$ -dibenzoylphenylethylidenetetrazen,  $\text{CHMe:N:NPh:Nbz:NHBz}$ , lustrous yellow needles, m. p. 158°, and  $\alpha$ -dibenzoylphenylethylidenetetrazen, yellow needles, m. p. 144—145°. The  $\beta$ -variety readily passes into the  $\alpha$ -isomeride under the influence of ammonia in alcoholic solution. Either form is converted by hydrochloric acid in the presence of alcohol into dibenzoylhydrazinooacetaldehydephenylhydrazone,  $\text{NHPh:N:COEt:Nbz:NHBz}$ , needles, m. p. 178—179°.

Acetophenone- and benzophenone-phenylhydrazones do not appear to react with azodibenzoyl.

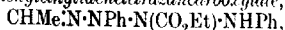
The catalytic aid of hydrogen is necessary for the combination of hydrazones with ethyl phenylazocarboxylate. The latter substance unites with benzaldehydephenylhydrazone to give ethyl  $\beta\delta$ -diphenyl- $\alpha$ -benzylidenetetrazen- $\gamma$ -carboxylate,



yellow needles, m. p. 124—125° (slight decomp.). It is readily reduced by zinc dust and acetic acid to ethyl phenylhydrazine-carboxylate and benzaldehydephenylhydrazone. It is relatively very stable towards acids. When treated with a little potassium hydroxide in the presence of alcohol it is converted into 4-anilino-

1:3-diphenyltriazolone,  $\text{NPh:CO} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{CPh} > \text{N:NPh}$ , lustrous needles, m. p.

175°. Ethyl diphenylethylidenetetrazen-carboxylate,



crystallises in yellow needles, m. p. 105—106°; it is obtained from either form of the acetaldehydephenylhydrazone. It is moderately stable towards mineral acids, but appears to be converted by alkali hydroxide into a formazyl derivative which could not be caused to crystallise.

Phenylazoacetaldehydeoxime shows the least tendency among acylazo-compounds to yield tetrazans. It unites, however, with  $\beta$ -acetaldehydephenylhydrazone in ethereal solution in the presence of a little acetic acid to give *diphenylethylidenetetrazanacetaldehyde-oxime*,  $\text{CHMe:N}\cdot\text{NPh}\cdot\text{N}(\text{CMe:N}\cdot\text{OH})\cdot\text{NHPh}$ , orange-yellow needles, m. p.  $83^\circ$ ; under the influence of glacial acetic acid, this compound is also produced from  $\alpha$ -acetaldehydephenylhydrazone.

*Diphenylethylidenetetrazancarboxylamide*,

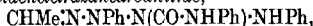


yellow leaflets, m. p.  $164^\circ$ , is produced from phenylazocarboxylamide and  $\beta$ -acetaldehydephenylhydrazone in neutral, alcoholic solution or from the corresponding  $\alpha$ -compound in the presence of a trace of hydrochloric acid. It is converted in boiling alcoholic solution to which a little potassium hydroxide or hydrochloric acid has been

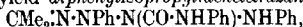
added into 4-anilino-1-phenyl-3-methyltriazolone,  $\text{NPh}\cdot\text{CO}\cdot\text{N}=\text{CMe}\cdot\text{N}\cdot\text{NHPh}$ ,

small, colourless needles, m. p.  $148^\circ$ ; the corresponding *nitroso*-derivative crystallises in pale yellow needles, m. p.  $68^\circ$ .

*Diphenylethylidenetetrazancarbanilide*,

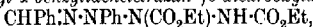


lustrous, yellow needles, m. p.  $158^\circ$ , is most conveniently prepared by heating acetaldehydephenylhydrazone and phenylazocarbanilide on the steam-bath until a clear, molten product is obtained. It is converted by boiling alcoholic hydrogen chloride into 2-acetyl-1:4-diphenylsemicarbazide,  $\text{NHPh}\cdot\text{N}\cdot\text{Ac}\cdot\text{CO}\cdot\text{NHPh}$ , colourless needles, m. p.  $179\text{--}180^\circ$ . *Diphenylbenzylidenetetrazancarbanilide*,  $\text{CHPh:N}\cdot\text{NPh}\cdot\text{N}(\text{CO}\cdot\text{NHPh})\cdot\text{NHPh}$ , crystallises in small, yellow needles, m. p.  $133^\circ$  (decomp.). It is transformed by alcoholic potassium hydroxide solution into diphenylanilino-triazolone, m. p.  $175\text{--}176^\circ$ , and a formazyl derivative which was not isolated in a homogeneous condition. Acetonephenylhydrazone and phenylazocarbanilide yield *diphenylisopropylidenetetrazancarbanilide*,



small, yellow needles, m. p.  $150^\circ$  (decomp.) in small yield.

*Ethyl  $\beta$ -phenyl- $\alpha$ -benzylidenetetrazan- $\gamma$ -dicarboxylate*,



pale lemon-yellow needles, m. p.  $106^\circ$ , is readily prepared from benzaldehydephenylhydrazone and ethyl azodicarboxylate. It is readily converted by alkali hydroxides or mineral acids into *ethyl ketodiphenyltetrahydrotetrazinecarboxylate*,  $\text{CO}_2\text{Et}\cdot\text{N}\cdot\text{N}(\text{CPh}=\text{N})\cdot\text{NH}\cdot\text{CO}$ ,  $\text{NPh}$ ,

colourless, lustrous leaflets, m. p.  $149\text{--}150^\circ$ , which is indifferent towards nitrous acid and highly resistant towards hydrolysis. *Ethyl  $\beta$ -phenyl- $\alpha$ -m-nitrobenzylidenetetrazan- $\gamma$ -dicarboxylate*, yellow prisms, m. p.  $159\text{--}160^\circ$  (decomp.), is converted in a similar manner into *ethyl ketophenyl-m-nitrophenyltetrahydrotetrazinecarboxylate*,

colourless needles, or hexagonal leaflets, m. p.  $179\text{--}180^\circ$ . *Ethyl  $\beta$ -phenyl- $\alpha$ -o-hydroxybenzylidenetetrazan- $\gamma$ -dicarboxylate* forms pale yellow crystals, m. p.  $147\text{--}148^\circ$ , depending on the rate of heating, whereas *ethyl ketophenyl-o-hydroxyphenyltetrahydrotetrazinecarboxylate* crystallises in aggregates of needles, m. p.  $184\text{--}185^\circ$ . *Ethyl*

*p*-phenyl- $\alpha$ -ethylidenetetrazen- $\gamma$ -dicarboxylate is obtained from  $\alpha$ - or -acetaldehydophenylhydrazones as a viscous, red liquid, which is converted by hydrochloric acid into ethyl ketophenylmethyltetrahydrotriazinecarboxylate, small, colourless needles, m. p. 112°. Ethyl azodicarboxylate does not show any tendency to unite with ketonehydrazones.

Ethyl  $\beta$ -o-tolyl- $\alpha$ -benzylidenetetrazen- $\gamma$ -dicarboxylate, yellow prisms or plates, m. p. 145° (or +C<sub>6</sub>H<sub>6</sub>, m. p. 112—113°), is converted by potassium hydroxide or hydrochloric acid in alcoholic solution into ethyl ketophenyl-o-tolyltetrahydrotriazinecarboxylate, colourless, lustrous needles, m. p. 93—94° after softening at 90°. Ethyl  $\beta$ -o-tolyl-hydroxybenzylidenetetrazen- $\gamma$ -dicarboxylate crystallises in small, yellow prisms, m. p. 104—106°, whereas ethyl keto-o-hydroxyphenyl-tolyltetrahydrotriazinecarboxylate forms colourless needles, m. p. 78°.

H. W.

**The Behaviour of the Most Important Proteins, Ferments, and Toxins towards Aluminium Hydroxide.** M. A. RAKUZIN *Ber.*, 1923, 56, [B], 1385—1388).—Amphoteric aluminium hydroxide does not behave exclusively as an adsorbent towards the most important proteins. Normal adsorption occurs only with the casein molecule; in other cases, fission of the protein molecule is usually observed. Very characteristic decomposition is observed with technical pepsin, chondrin, and antidiphtheric serum, which leads to the isolation of pure substances and to their quantitative estimation (cf. A., 1917, i, 181, 427). In general, the processes occur quantitatively within twenty-four hours if anhydrous aluminium hydroxide is employed; otherwise adsorption is not complete even in aqueous solution. The action of aluminium hydroxide is due to its amphoteric nature, since ferric hydroxide oxide has no action on similar solutions under identical conditions. Towards alcoholic extracts aluminium hydroxides exert a peculiar selective action, causing the successive elimination of complex ester complex from the protein derivatives down to the associated crystalline carbohydrates.

H. W.

**The Hydrolysis of Proteins by Dilute Acids.** N. ZELINSKI and W. SADIKOV (*Biochem. Z.*, 1923, 138, 156—160).—Catalytic hydrolysis of proteins is effected by the use of dilute hydrochloric acid (1—2%) at 180° in an autoclave. Hydrolysis is as complete in two to six hours as when excess of strong acids is used at lower temperatures and for longer periods, and little or no coloured decomposition products are formed. Whole organs and small live animals (mice, guinea-pigs, small dogs, and cats) treated in this way are completely broken down, and in addition to the usual amino-acids and peptides, anhydrides (diketopiperazines) have been obtained. The hydrolytic product thus prepared from whole organs is a convenient nutrient medium for bacteria. J. P.

**Amount of Tryptophan in Various Proteins.** YOSHIHIKO ATSUYAMA and TAKEJIRO MORI (*J. Chem. Soc. Japan*, 1923, 44, 7—381).—The authors have improved May and Rose's method estimating tryptophan (this vol., i, 160). 0.1 G. of the sample

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is placed in an Erlenmeyer flask, 2 c.c. of 0.2% sodium hydroxide solution are added; the flask is warmed at 40–50°, cooled; 100 c.c. of hydrochloric acid (1 : 1) and 1 c.c. of Ehrlich's reagent are added, heated at 25° for twenty-four hours, and set aside for twenty-four to forty hours. The blue colour thus produced is compared with that of casein, treated in the same manner, assuming the content of tryptophan in casein to be 1.5%. Estimations of tryptophan in various proteins by the old and new methods respectively gave the following results: beef protein, 1.20, 1.28; tunny protein, 1.18, 1.01; salmon protein, 1.03, 0.92; scallop protein, 1.18, 1.09; syntonin, 0.63, 0.82; serum-albumin, 1.62, 1.45; fibrin, 1.71, —; hæmoglobin, 1.80, —; egg albumin, 1.18, 1.11; fibroin, trace, trace; mucin, 0, 0; gelatin, 0, 0; globulin, 1.62, 1.52; soja bean protein, 0.82, —; rice protein, 1.33, —; edestin, 1.46, 1.40; legumin, 0.94, 0.67; conglutin, 1.45, 1.28; wheat gluten, 1.00, 0.95; zein, 0, 0; protein of *Fagopyrum esculentum*, 0.68, 0.83%; and protein of pine nut, 0, trace.

K. K.

**Preparation of Tryptophan from the Products of Hydrolysis of Lactalbumin with Baryta.** HENRY C. WATERMAN (*J. Biol. Chem.*, 1923, **56**, 75–77).—The lactalbumin (200 g.) is hydrolysed by heating at about 85° for forty hours with a solution of baryta (700 g.) in water (4 litres). The tryptophan is then isolated from the product by means of Hopkins and Cole's mercuric sulphate reagent. Baryta hydrolysis possesses certain advantages over trypsin digestion; it is quicker and it renders the isolation process simpler since cystine is destroyed.

E. S.

**Effect of Ultra-violet Rays on Protein Solutions.** RUDOLF MOND (*Pflüger's Archiv*, 1922, **196**, 540–559; from *Chem. Zentr.*, 1923, i, 559).—Ultra-violet radiation increases the stability of globulin and fibrinogen solutions, whilst the stability of albumin solutions is diminished. The reaction of serum-globulin and albumin solutions is rendered more acid, whilst the surface tension shows a decrease which is least in the case of albumin. Viscosity increases owing, probably, to the formation of aggregates.

G. W. R.

**A Spontaneous Crystallisation of a Bence-Jones Protein.** D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, **56**, 203–214).—A case is recorded in which a Bence-Jones protein crystallised spontaneously from the urine. Of the total nitrogen of the protein, 4.86% was present as free amino-nitrogen; this small percentage is additional evidence in favour of classing the compound as a protein and not as an albumose.

E. S.

**Physical Chemistry of the Proteins. II. The Relation between the Solubility of Casein and its Capacity to Combine with Base. The Solubility of Casein in Systems containing the Protein and Sodium Hydroxide.** EDWIN J. COHN and JESSIE L. HENDRY (*J. Gen. Physiol.*, 1923, **5**, 521–553; cf. A., 1922, i, 882).—Measurements have been made of the solubility

of highly purified casein in solutions of sodium hydroxide. It appears that the solubility represents the sum of the solubility of the protein molecule itself along with that of the caseinate-ion, which would seem to be doubly charged. On these assumptions, it is found that the solubility of casein is approximately 0.09 g. per litre at 25°, and that the product of the two dissociation constants of casein,  $K_a$  and  $K_b$ , is  $24 \times 10^{-12}$ . Each gram-molecule of sodium hydroxide combines with 2100 g. of casein. W. O. K.

**A New Sulphur-containing Amino-acid Isolated from the Hydrolytic Products of Protein.** J. HOWARD MUELLER (*J. Biol. Chem.*, 1923, 56, 157—169).—The sulphur-containing product isolated from the hydrolytic products of casein, which appeared to be required for growth by hæmolytic streptococci (*J. Bact.*, 1922, 7, 309, 325), has been found to lose its growth-promoting properties on purification. The pure substance is an amino-acid,  $C_5H_{11}O_2NS$ , hexagonal plates, m. p. (decomp.) 283° (uncorr.) after darkening at 278°,  $[\alpha]_D^{20} -7.2^\circ$  in aqueous solution (partial racemisation may have occurred during the extraction process), and is isomeric with ethyleysteine. It forms a naphthylcarbamido-derivative, short needles, m. p. 186° (uncorr.), a copper salt,  $(C_5H_{10}O_2NS)_2Cu$ , hexagonal plates, and a precipitate with mercuric chloride which has approximately the composition  $(C_5H_{11}O_2NS)_2Hg_5Cl_8$ .

The isolation of the new amino-acid is troublesome owing to the difficulty of separating it from phenylalanine and glutamic acid. An isolation process has, however, been elaborated whereby yields of 0.2 to 0.4% have been obtained from casein, egg-albumin, elastin, and wool; gelatin gives much smaller yields. The isolation process is described in detail in the original; it consists essentially of hydrolysis of the protein by sulphuric acid or sodium hydroxide, precipitation of the amino-acid by mercuric sulphate, and, after recovery, precipitation by mercuric chloride. When recovered from the latter it is in a moderately pure condition; further purification, with considerable loss, may be effected by repeating the precipitation with mercuric chloride. The structure of the compound has not, so far, been determined. The sulphur is more firmly bound than in cysteine; it does not give the nitroprusside reaction, neither does it blacken lead. The amino-group is probably in the  $\alpha$ -position, since the nitrogen is given off quantitatively in three minutes in Van Slyke's apparatus. The evidence at present available points to the compound being a primary cleavage product of proteins.

E. S.

**Adsorption and Hæmoglobin.** A. V. HILL (*Nature*, 1923, 111, 843—844).—The specific colour changes which occur when reduced blood or hæmoglobin is shaken with oxygen or carbon monoxide support the theory of chemical change as against that of adsorption. The deduction from the phase rule that oxygen and reduced hæmoglobin are not separate chemical compounds is valid only if the hæmoglobin unit itself is a separate phase; this is purely hypothetical. Facts are briefly stated to show that the

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union of hæmoglobin with carbon dioxide is, in fact, of a different nature from that with oxygen (cf. Bayliss, this vol., i, 618).

A. A. E.

**Adsorption and Hæmoglobin.** N. K. ADAM (*Nature*, 1923, 111, 844—845).—A reply to Bayliss (this vol., i, 618). A. A. E.

**Valency Rule and Alleged Hofmeister Series in the Colloidal Behaviour of Proteins. I. The Action of Acids. II. The Influence of Salts.** JACQUES LOEB and M. KUNITZ (*J. Gen. Physiol.*, 1923, 5, 665—691, 693—707).—The previous work of Loeb is confirmed and extended. The influence of acids on the four properties of gelatin (membrane potentials, osmotic pressure, swelling, and viscosity) depends on the valency and strength of the acid and not on the particular anion. If the  $p_H$  is taken into account, the Hofmeister series is not valid. In the same way, on the acid side of the isoelectric point, the effect of salts depends on the valency of the anion and not on its chemical nature, and not at all on the kation.

W. O. K.

**The Theory of Negative Adsorption. III. The Adsorption of Sodium Chloride and other Compounds by Gelatin.** M. A. RAKUZIN and (Mlle) TATIANA ALFR. HENKE (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 248—256).—In order to test the well-established view that dry gelatin absorbs water when brought into contact with aqueous solutions of different substances and thus causes an increase in the concentration of the solution, 3% by weight of dry gelatin was introduced into a variety of aqueous solutions of both crystalloids and colloids. It was found in all cases that although the concentration of the solution rose after twenty-four hours' contact with gelatin, the increase was due to the passage of gelatin into the solution; this was confirmed by careful experiments on the action of gelatin on solutions of sodium chloride at different concentrations; in no case could the crystallisation of a saturated salt solution be induced by contact with gelatin. Attempts to induce the crystallisation of saturated solutions of ammonium chloride and barium chloride by the repeated addition of gelatin (up to 9%) were equally unsuccessful. G. A. R. K.

**The Theory of Negative Adsorption. IV. The Action of Gelatin on some Acids.** M. A. RAKUZIN and (Mlle) TATIANA ALFR. HENKE (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 256—258).—Using an experimental method similar to that previously described (preceding abstract), the authors have studied the action of gelatin on solutions of four inorganic and five organic acids. The results clearly suggest an interaction, probably with the formation of salt-like complexes, in all the cases examined.

G. A. R. K.

**An Albumose from Wool.** LEON MARCHLEWSKI and (Mlle) A. NOWOTNÓWNA (*Zjazd Chemików Polskich*, 1923, 26).—A small amount of albumose, giving all the ordinary reactions of albumoses, is obtained by the hydrolysis of wool with solutions of calcium or barium hydroxide.

R. T.

**The Active Principle of Pepsin.** M. A. RAKUZIN and S. L. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 234—242).—The extraction of dry preparations of pepsin with 95% alcohol for three days leads to a loss in weight of 87.46%. The insoluble residue is nitrogenous and has proteolytic properties, its activity being about one-half that of the original pepsin, in spite of the prolonged heating with alcohol. The portion soluble in alcohol is non-nitrogenous, has no action on proteins, and is shown to consist of inositol; it has m. p. 176—177°,  $[\alpha]_D +45.35^\circ$  after purification.

The nitrogenous constituent of pepsin can, apparently, also be separated from pepsin solutions by adsorption by means of alumina, a constant fraction of the original solid (12.4%) being removed from the solution, and the carbohydrate constituent being left.

The nitrogen in the active principle of pepsin appears to be combined in the form of lecithin or nucleoprotein. G. A. R. K.

**The Products of the Digestion of Blood Pigment by Pepsin.** A. DMOCHOWSKI (*1<sup>ty</sup> Zjazd Chemików Polskich*, 1923, 58—59).—Quantitative determinations are made of the products of digestion with pepsin of blood and of oxyhæmoglobin derived from horse blood. The production of digestive hæmatin from the latter is found to be 4.3%, thus confirming the results of Schultz and Zawrow. It was not found possible to determine quantitatively the percentage of hæmatin produced from blood, owing to the difficulty of separating fatty and cellular materials from the latter.

R. T.

**The Effect of Radioactive Radiations and X-Rays on Enzymes. I. The Effect of Radiations from Radium Emanation on Solutions of Trypsin.** RAYMOND G. HUSSEY and WILLIAM R. THOMSON (*J. Gen. Physiol.*, 1923, 5, 647—659).—The decomposition of trypsin by radium emanation is a unimolecular reaction, and the rate of destruction is proportional to the concentration of trypsin and to the quantity of emanation.

W. O. K.

**Hydrolysis of Collagen by Trypsin.** ARTHUR W. THOMAS and F. L. SEYMOUR-JONES (*J. Amer. Chem. Soc.*, 1923, 45, 1515—1522).—A study has been made of the hydrolysis of collagen by means of trypsin, by controlling the acidity during digestion and re-treatment, and examining the effects of varying the time of digestion, concentration of enzyme, and size of the collagen particles. The optimum hydron concentration for the hydrolysis is found to be at  $P_H$  5.9. Pre-treatment of the collagen in solutions of various degrees of acidity does not influence the subsequent typical digestion. The speed of hydrolysis increases as the size of the collagen particles decreases, the reaction probably occurring at the surface. Hydrolysis increases with increasing concentration of trypsin, but is never complete under the limits of experimental conditions. The hydrolysis-time curve shows slight reversibility. It is pointed out that the hydrolysis of soluble proteins by means of trypsin is probably a surface reaction, the proteins being merely colloidal dispersed, rather than in true solution.

W. S. N.

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**The Composition and Properties of Papain.** M. A. RAKUZIN and S. L. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 243—247).—Papain differs from pepsin in giving the Adamkiewicz reaction for tryptophan; the Ostromisslenski reaction, which pepsin gives to a small extent, is well marked, whilst Molisch's reaction is common to both ferments; the Liebermann reaction is negative. The rotation of papain is  $+32.9^\circ$ . Its behaviour towards organic "tanning" agents is characteristic: formaldehyde, phenol, and  $\alpha$ -naphthol react with the whole of the nitrogen, and the solution after treatment with these reagents still gives a coloration with Molisch's reagent for carbohydrates, but the Adamkiewicz and Ostromisslenski tests are negative. Picric acid reacts only with tryptophan, affecting the Adamkiewicz test alone;  $\beta$ -naphthol has no action on papain.

Papain contains no iron; chlorine, phosphorus, and sulphur (as cystine) are present. Unlike pepsin, papain is not adsorbed by alumina. Extraction of the dry substance with 95% alcohol removes 69%; the residue does not give the Ostromisslenski reaction; the extract contains a crystalline substance melting at  $179^\circ$ .

G. A. R. K.

**Enzyme Action. XXIII. The Spontaneous Increase in Saccharase Activity of Banana Extracts.** GRACE MCGUIRE and K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1923, **45**, 1539—1551).—The saccharase extracts are prepared by grinding banana pulp with solutions of different salts, the ratio of g. of pulp to c.c. of solution being 2:1. During the slow filtration of the mixture toluene is generally added as a preservative; the extracts are subsequently dialysed to remove most of the salts. The saccharase action, as measured by incubating the enzyme preparation, suitably diluted, with sucrose solutions for one to four hours at  $37.5^\circ$ ,  $0.05^\circ$ , and determining the reducing substances with Fehling's solution, increases on keeping, even at low temperatures ( $5-10^\circ$  from 40—100%, and then decreases. This behaviour is independent of the composition of the extracting solution, or of the preservative used. Banana cells and bacteria are absent during the period of change. An alteration in the hydrogen-ion concentration is insufficient to account for the phenomenon, because an extract made using 0.6*M*-magnesium sulphate, filtered during less than one hour, and dialysed for two to three hours against tap water, had  $P_H$  5.0, and no change in this value, as measured by means of indicators, could be detected on keeping. That the change in hydrogen-ion concentration, necessary to account for the increase in activity, could be detected by means of the indicators used is shown by a series of experiments, using the extract mentioned in which the effect, on the ageing of the extract, of added hydrochloric acid, sodium hydroxide solution, or citrate buffer solution is studied. A previous observation (*J. Gen. Physiol.*, 1921, **3**, 595; *J. Biol. Chem.*, 1922, **54**, 655), that for the maximum saccharase activity of banana extracts there is an optimum  $P_H$  value between 3.5 and 5.0, is confirmed.

The explanation favoured is that banana extracts contain material which "spontaneously" forms new enzyme, but that, once formed, banana saccharase loses its activity steadily. This accounts both for the initial increase and for the occurrence of a maximum of activity.

W. S. N.

## Lipase. II. A Comparison of the Hydrolysis of the Esters of the Dicarboxylic Acids by the Lipase of the Liver.

ELIZABETH C. HYDE and HOWARD B. LEWIS (*J. Biol. Chem.*, 1923, 86, 7—15).—Ethyl glutarate and ethyl adipate are completely hydrolysed by lipase from pig's liver, thus differing from ethyl malonate and ethyl succinate, which are only hydrolysed as far as the half ester (cf. Christman and Lewis, A., 1921, i, 755). If, in the case of the two former esters, the acid liberated in the early stages of the hydrolysis is neutralised with sodium hydroxide, the reaction stops when 50% of the ester has been hydrolysed. Adipic acid was isolated from the product in such a case. The rates of hydrolysis by lipase of the above four esters increase with the molecular weight of the ester.

E. S.

## Existence of Arsino-magnesium Compounds. ANDRÉ JOB

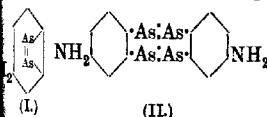
and RENÉ REICH (*Compt. rend.*, 1923, 177, 56—58).—Phenylarsine (1 mol.) and magnesium ethyl bromide (2 mols.) interact in etheral solution to give ethane (2 mols.) and the oily *arsino-magnesium* compound,  $\text{AsPh}(\text{MgBr})_2$ . This substance, which is readily oxidised, and is decomposed by water to give phenylarsine, is apparently converted by carbon dioxide into the compound,  $\text{AsPh}(\text{CO}_2\text{MgBr})_2$ , which is decomposed even by water, generating the arsine. Ethyl chloroformate converts the *arsino-magnesium* compound into the *ester*,  $\text{AsPh}(\text{CO}_2\text{Et})_2$ , a colourless liquid, b. p. 180—183°/20 mm., and apparently stable in air. Hydrolysis with alkali regenerates phenylarsine.

E. E. T.

## Aromatic Diarsinic Acids and their Reduction Products.

L. H. LIEB and O. WINTERSTEINER (*Ber.*, 1923, 56, [B], 1283—1291).—A continuation of previous work (cf. Lieb, A., 1921, 396; Lieb and Wintersteiner, this vol., i, 408).

4-Nitrophenylene-1:2-diarsinic acid,  $\text{NO}_2\text{C}_6\text{H}_3(\text{AsO}_3\text{H}_2)_2\text{H}_2\text{O}$ , as prismatic needles, is prepared by diazotising 5-nitro-2-aminophenylarsinic acid and treatment of the product with alkaline sodium arsenite solution in the presence of a little copper powder; it is conveniently purified by means of the zinc salt. When heated above 100° it passes into the corresponding *anhydride*. The nitro-group is reduced by ferrous chloride to 4-aminophenylene-1:2-diarsinic acid,  $\text{C}_6\text{H}_4\text{O}_6\text{NAs}_2\text{H}_2\text{O}$ , the zinc salt and the *anhydride* of which have been prepared. Complete reduction of the amino-acid



(II)

by hypophosphorous acid leads to the production of 4-amino-1:2-arsenobenzene or 4:4'-diamino-1:2:1':2'-diarsenodibenzene (annexed formulæ I or II), a yellow, amorphous

substance, the hydrochloride of which is described. The decision

between the alternative formulæ could not be effected by determinations of the molecular weight, since it yields a colloidal solution in pyridine, which is the only available solvent.

*2-Hydroxyphenylene-p-diarsinic acid*, colourless or pale pink rhombic leaflets, which becomes discoloured at 220°, but does not melt or decompose below 315°, is obtained by diazotising 2-aminophenylene-*p*-diarsinic acid and heating the product with water. When reduced with hypophosphorous acid, it gives *2-hydroxy-1:4:arsenobenzene* or *2:2'-dihydroxy-1:4:1':4'-diarsenodibenzene*, a reddish-brown, amorphous substance which is fairly stable towards air when dry, but is exceptionally readily oxidised in solution.

*2-Chlorophenylene-p-diarsinic acid*,  $C_6H_4O_6ClAs_2 \cdot 0.5H_2O$ , colourless, rhombic leaflets which soften and become discoloured at 210° but do not melt below 315°, is prepared by the action of copper bronze on a diazotised solution of 2-aminophenylene-*p*-diarsinic acid in the presence of hydrochloric acid, and is purified conveniently by means of its zinc salt. It may be also obtained by diazotising 3-chloro-4-aminophenylarsinic acid and coupling the product with sodium arsenite, but the yields are very poor. It is reduced by hypophosphorous acid to an amorphous, yellow product which appears to be *2-chloro-1:4:arsenobenzene* or *2:2'-dichloro-1:4:1':4'-diarsenodibenzene*.

*2-Bromophenylene-p-diarsinic acid*,  $C_6H_4O_6BrAs_2 \cdot 0.5H_2O$ , is prepared in the same manner as the corresponding chloro-derivative  
H. W.

#### Preparation of Hydroxides and Oxides of Triarylstibine

LUDWIG KAUFMANN (D.R.-P. 360973; from *Chem. Zentr.*, 1923, ii, 336).—Triarylstibines, in solution or in suspension, are treated with peroxides in the presence or absence of catalysts such as metals, salts, or metallic oxides. For example, triphenylstibine gives with 3% hydrogen peroxide in the presence of dilute potassium hydroxide solution, or with sodium peroxide, *triphenylstibine hydroxide*; it forms crystals, m. p. 212°. *p-Tritolylstibine hydroxide* has m. p. 225°; the *acetate* has m. p. about 165°.

G. W. R.

### Physiological Chemistry.

**Physiological Action of Proteinogenic Amines. VII. The Influence of Di-iodotyrosine, Di-iodotyramine, and Hordenine on the Gaseous Exchange.** J. ABELIN (*Biochem. Z.*, 1923, 138, 161—168).—Tables are given showing the effect of oral and subcutaneous administration of di-iodotyrosine, di-iodotyramine, and hordenine (*ω*-dimethyltyramine) on the gaseous exchange of the white rat. In contrast to tyramine (cf. A., 1920, i, 264; A., 1922, i, 610), di-iodotyrosine and di-iodotyramine have little or no influence on the gaseous metabolism. The oral adminis-

tration of hordenine produces a diminution in the exchange, thus acting in the same way as tyramine, phenylethylamine, and adrenaline. J. P.

**The Reduction of Nitro-groups by Living Tissues.** WERNER LIPSCHITZ (*Biochem. Z.*, 1923, 138, 274—278).—A reply to the criticisms by Waterman and Kalf (this vol., i, 415), of the author's results on the reduction of *m*-dinitrobenzene by excised tissues and tumours (*A.*, 1921, i, 203). J. P.

**The Phosphorus Compounds in Normal Blood.** MARY V. BUELL (*J. Biol. Chem.*, 1923, 56, 97—107).—Analyses have been made of the phosphorus content of human blood and of blood from normal dogs, precautions being taken to prevent changes in the distribution between the corpuscles and plasma after collection. The results indicate that, in the living organism, the inorganic phosphate of the blood is present only in the plasma, and the organic phosphate only in the corpuscles. E. S.

**Chemical Factors in Fatigue. II. Further Changes in some of the Blood Constituents following Strenuous Muscular Exercise.** NORRIS W. RAKESTRAW [with CHARLES V. BARLEY and YOUNG D. HAHN] (*J. Biol. Chem.*, 1923, 56, 121—124; cf. *ibid.*, 1921, 47, 565).—Short periods of strenuous exercise are followed by increases in the uric acid and sugar content of the blood. The increase in the former substance continues for more than one and a half hours after exercise; the sugar, however, falls to a value below normal in this time. Slight increases have also been observed in the chloride content; that of amino-acids and free and conjugated phenols remains unchanged. E. S.

**Variations in the Distribution of the Non-protein Nitrogenous Constituents of Whole Blood and Plasma during Acute Retention and Elimination.** E. D. PLASS (*J. Biol. Chem.*, 1923, 56, 17—29).—Analyses have been made of the non-protein nitrogenous constituents of whole-blood and plasma during pregnancy and eclampsia. The results indicate that these constituents diffuse into the corpuscles during periods of retention and again return to the plasma when their concentration in the latter has been reduced by improved elimination. E. S.

**Is Pyruvic Acid a Stage in the Decomposition of Dextrose during Glycolysis?** J. SIMON and E. AUBEL (*Compt. rend.*, 1923, 176, 1925—1927).—Pyruvic acid is not a normal constituent of the blood of animals, whether fasting or on full diet, neither is sodium pyruvate decomposed by blood in vitro more rapidly than by water. Pyruvic acid is not produced during glycolysis, and therefore cannot be an intermediary between dextrose and lactic acid. E. E. T.

**Relation between Hæmoglobin-content and Surface of Red Blood-cells.** E. GORTER (*Nature*, 1923, 111, 845).—A consideration of the mode of distribution of hæmoglobin molecules in red blood-cells. A. A. E.

**Origin and Nature of Thrombin.** P. NOLF (*Arch. Néerland physiol.*, 1922, 7, 348—351; from *Chem. Zentr.*, 1923, i, 619).—Blood plasma is a mixture of proteins of various origin, including thrombozymes from the white blood corpuscles and endothelial cells outside the liver, and other proteins (fibrinogen, thrombogen, antithrombosin, and antithrombolysin) secreted by the liver. Both groups include albumins and globulins. Coagulation, which consists of the combination of thrombozyme with liver proteins, does not take place when the least soluble thrombozyme (thrombozyme globulin) and the least soluble liver protein (fibrinogen) are brought together, but is facilitated by the presence of the more soluble thrombogen. There is an excess of slightly soluble liver proteins in plasma. Of the complexes formed by coagulation, one part contains fibrinogen and fibrin and the other part (thrombin) little or no fibrinogen. The thrombin of normal serum is a soluble fibrin which forms an insoluble fibrin with fibrinogen or, more slowly, with the more easily soluble liver colloids with formation of meta-thrombin ( $\beta$ -proferment of Morawitz).  
G. W. R.

**Chemical Constituents of Saliva as Indices of Glandular Activity.** J. LUCIEN MORRIS and VERNON JERSEY (*J. Biol. Chem.*, 1923, 56, 31—42).—Estimations have been made of the urea, ammonia, amino-nitrogen, creatinine, and uric acid content of human saliva collected in successive half-hour periods from resting glands and from glands stimulated into activity by chewing. Similar estimations have been made following the ingestion of acetic acid, pilocarpine, and atropine. The different effects of the various stimuli on the volume and composition of the saliva indicate that several factors are involved in the elaboration of the secretion.  
E. S.

**The Rôle of Oxyproteic Acids in the Acidity of the Human System.** STANISŁAW BADZYŃSKI and WAĆŁAW KARCZEWSKI (*Więści Zjazd Chemików Polskich*, 1923, 52—53).—The view that the action on proteins is the same in the intestines as in the body-cells is shown to be incorrect; in the former case, the only action is hydrolysis to amino-acids, whilst in the latter case, this is preceded by oxidation. That the oxyproteic acids produced by the latter process are highly oxidised is shown by the very high silver or barium content of their salts; the oxygen content is from 1.4 to 2 times as high as that of the proteins from which they are derived. The excretion of oxyproteic acids is increased by the addition of larger quantities of proteins to the diet, by bacterial poisoning or by poisoning with carbon monoxide, chloroform, ether, atophan etc. The average daily excretion of these acids is calculated to be 4.85 g., and the quantity of alkali removed from the body, combined with the acids, is equivalent to 241—376 c.c. of  $N/10$ -sodium hydroxide solution.  
R. T.

**Influence of the Condition of Acidosis on the Metabolism of the Alkaline-earth Metals of the Organism.** MICHEL FLORIS (*Arch. Farm. speriment. Sci. aff.*, 1923, 35, 88—96, 97—103, 113—121, 129—138, 145—153, 161—166).—The author gives a

summary of previous work on the biological and pharmacological action of calcium and magnesium compounds, and on the interchanges of these compounds both after administration of acids and during a condition of pathological acidosis. The results of his own experiments on dogs show that ingestion per day of 5 c.c. of lactic acid or 0.89 c.c. per kg. of body-weight, extending over a period of five days, produces a marked diminution in the proportions of calcium and magnesium in the faeces and a slight increase in those in the urine. Both calcium and magnesium are retained to an appreciable extent by the organism. A daily dose of 1.37 c.c. of the acid per kg. of body-weight for four days caused increases in the faecal and urinary elimination of the lime and impoverishment of the organism; the elimination of magnesia by the faeces diminished and that by the urine increased, the balance being in favour of the organism. Ingestion of lactic acid reproduces especially those conditions in which, owing to abnormal fermentation, organic acids are produced in considerable proportions in the digestive tract, and causes an analogous loss of calcium by the organism.

T. H. P.

**Creatine and Creatinine Metabolism. V. The Metabolism of Creatine.** STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1923, **56**, 229–252).—Although the view, originally expressed by Folin, that urinary creatinine is not derived from creatine has from time to time been questioned (cf. for example, Rose and Dimmitt, A., 1916, i, 774; Behre and Benedict, A., 1922, ii, 789), decisive evidence against it has not hitherto been forthcoming. A survey of the literature has shown that, in experiments which apparently support this view, the creatine administered to the animals employed has not been accounted for in any way. Experiments have accordingly been carried out in which small amounts of creatine were fed daily for long periods to dogs, initially in approximate nitrogen equilibrium, estimations being made of the creatine and creatinine eliminated. During roughly the first week, no effect on the elimination of these substances was observed; thereafter, however, increased amounts of both were excreted, until finally approximately 50% of the creatine administered in a given period was eliminated unchanged. At the same time, there was a large retention of nitrogen and two out of the three animals increased considerably in weight. When the administration of creatine was stopped, there was an immediate cessation in the elimination of this substance; creatinine, on the other hand, continued to be excreted in amounts considerably larger than normal. When the urinary creatinine again reached a normal figure, it was found that, in each case, the amount of additional creatinine excreted during the whole experimental period corresponded with approximately one-third of the creatine otherwise unaccounted for. These results appear to indicate that creatine is metabolised extremely slowly and in two distinct ways, one of which yields, apparently indirectly, creatinine. On this basis, two distinct types of creatinuria should exist: one due to an excess of creatine

in the organism, and the other due to a failure to utilise that portion of the creatine which normally does not yield creatinine. E. S.

**Pyrimidine Metabolism.** D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, 56, 215—227).—Experiments on rabbits and man show that, although free uracil is not attacked in the body, when administered in the form of a nucleoside or a nucleotide it is to a large extent destroyed, only a small portion being excreted unchanged; when administered as yeast-nucleic acid, it is completely destroyed. Hence the first step in the metabolism of nucleic acid is some change in the pyrimidine group, which evidently precedes hydrolysis into the nucleotides. E. S.

**Aqueous Extracts of Pancreas. I. Influence on the Carbohydrate Metabolism of Depancreatized Animals.** JOHN R. MURLIN, HARRY D. CLOUGH, C. B. F. GIBBS, and ARTHUR M. STOKES (*J. Biol. Chem.*, 1923, 56, 253—296; cf. Banting, Best, Collip, Macleod, and Noble, this vol., i, 420).—Preparations of insulin made by extracting the pancreas with 0.2N-hydrochloric acid and subsequently neutralising with sodium hydroxide have as great an effect on the blood sugar and the dextrose : nitrogen ratio of depancreatized animals as those prepared by extraction with alcoholic hydrochloric acid according to the method of Banting and Best. Extremely toxic effects result from the administration of such preparations unless the acid is previously neutralised and the trypsin completely destroyed.

A rise in the respiratory quotient and a considerable utilisation of sugar have been observed in depancreatized animals (dogs) following the administration by the stomach of extracts of ox pancreas; the minimal dose which produced this effect was equivalent to about 125 g. of the pancreas.

Acid extracts of pancreas may be boiled for at least five minutes without destroying the insulin. This substance is, however, largely removed by filtration of the extracts through charcoal or Lloyd's reagent.

It is stated that the above aqueous extracts of pancreas contain, in addition to insulin, a substance which produces a rise in the blood-sugar of both normal and diabetic animals, but details are reserved for a future publication. E. S.

**Boron in Animal Organs.** GIUSEPPE MOSCATI (*Arch. Sci. biol.*, 1922, 3, 279—288; from *Chem. Zentr.*, 1923, i, 362).—Boron occurs in human organs, the minimum amount being present in the liver and the maximum amount in the kidneys. It occurs also in foetal liver and spleen. Urine also contains boron. In the case of a dog, administration of borax resulted in the presence of boron in the blood and all organs. G. W. R.

**Chemistry of the Oils of Marine Animals.** ÉMILE ANDRÉ (*Bull. Soc. chim.*, 1923, 33, [iv], 469—506).—Lectures given at the Collège de France. G. F. M.

**The Endothermic Reaction which Accompanies the Appearance of a Visible Curd in Milks Coagulated by Heat: A Contribution to the Theory of the Heat Coagulation of Milk.** ALAN LEIGHTON and COURTLAND S. MUDGE (*J. Biol. Chem.*, 1923, 56, 53—73).—The coagulation of casein produced by heating skimmed milk or evaporated skimmed milk is accompanied by an endothermic reaction which results, apparently, in the precipitation of calcium and magnesium as phosphates and citrates. The metals combined, as well as those uncombined, with the casein enter into this reaction.

The thickening of condensed milk is due to a chemical reaction and does not result from bacterial action. The effect of the degree of forewarming on the stability of both condensed and evaporated milk has been investigated in some detail. [Cf. *J.S.C.I.*, 1923, 737A.] E. S.

**Comparative Elimination of Total Nitrogen, Urea, Amino-acids, and of Ammonia during Waking Hours and during Sleep. I. Physiological Conditions. II. Total Starvation.** GEORGES FONTÈS and ALEXANDRE YOVANOVITCH (*Bull. Soc. Chim. biol.*, 1923, 5, 348—362, 363—371).—Analyses have been made of urine secreted during sleep and during waking hours under comparable conditions as regards food, activity, temperature of surroundings, etc. The excretion of water, total nitrogen, urea, and to a very slight degree of amino-acid nitrogen are decreased whilst that of ammonia and acidity to phenolphthalein is increased during sleep. Very similar results are obtained if food is not administered during the experiment. W. O. K.

**The Salicylates. XIV. Liberation of Salicyl from and Excretion of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.** P. J. HANZLIK and ELIZABETH PRESKO (*J. Pharm. Expt. Ther.*, 1923, 21, 247—261).—The rate of hydrolysis of *o*-acetoxybenzoic acid is minimum in neutral solution, but markedly increases if the reaction is slightly acid or alkaline. At  $p_H$  5.5, 34% is hydrolysed in eighteen hours, and at  $p_H$  8, 45%. Thus *o*-acetoxybenzoic acid ought to be fairly stable in buffer mixtures such as are encountered in the alimentary canal. This is verified by the fact that after administration of *o*-acetoxybenzoic acid, varying quantities, 5.3 to 41.1%, may be recovered from the urine. W. O. K.

**The Examination of the Blood of Pigeons suffering from Avitaminosis.** LEON MARCHLEWSKI and (MIL) A. NOWOTNÓWNA (*1<sup>st</sup> Zjazd Chemików Polskich*, 1923, 26).—The amount of non-albuminous nitrogen in the blood of pigeons suffering from avitaminosis is greater than the normal, pointing to an inability to synthesise proteins from amino-acids. R. T.

**Importance of Calcium and Potassium in the Pathological Physiology of Cancer.** MAURICE WOLF (*Compt. rend.*, 1923, 176, 1932—1934).—A study of the effect of calcium and potassium on the growth of an epithelioma of the mammary gland of the mouse. For normal (mouse) tissue, the ratio K/Ca varies from

5.41 (liver) to 0.053 (connective-tissue). For tissue infected with pneumococci, these values are respectively 4.21 and 1.51. For a rapidly and slowly developing epithelioma, respectively, the ratio is 20:15 and 5:10 (with occasional deviations within the limits of 57 and 0.049). Calcium retards and potassium stimulates growth. The former causes concentration, the latter dilution, of cytoplasm. Calcium is absorbed diffusely, potassium mainly in the neighbourhood of the nucleus.

E. E. T.

**Diphtheria Toxin. I. The Influence of Hydrogen-ion Concentration on Diphtheria Toxin.** FR. VON GRÖER (*Biochem. Z.*, 1923, 138, 13—33).—The addition of dilute hydrochloric acid, in appropriate amount, to diphtheria toxin produces a precipitate, soluble in excess of acid, which contains practically all the toxic principle. The zone of precipitation is broad and indefinite and lies on both sides of  $p_H$  5; precipitation is practically complete at  $p_H$  3— $p_H$  4. The toxin itself is regarded as analogous to an amphoteric electrolyte and shows a maximum toxicity at  $p_H$  8.5— $p_H$  9.2. At  $p_H$  5 and  $p_H$  12 it is inactive. In an addendum the author points out that his results accord qualitatively but not quantitatively with those of Walbum (*A.*, 1922, i, 902). J. P.

**Diphtheria Toxin. II. Investigations on the Formation of Toxin.** FR. VON GRÖER (*Biochem. Z.*, 1923, 138, 34—42).—Daily determinations were made of the alterations in hydrogen-ion concentration, optical rotation, refractive index, amino-nitrogen, and toxicity of actively growing diphtheria cultures. It is concluded that "actual" toxicity is dependent on the formation of new toxin, activation of the toxin by increasing alkalinity, and by autolysis of the toxin. The "absolute" toxicity of a culture is attained at  $p_H$  8.6—8.8.

J. P.

**Toxicity of a Polymeride of Hydrocyanic Acid.** CH. BEDÉL (*Compt. rend.*, 1923, 176, 1927—1929).—The tetrameride of hydrocyanic acid was purified as described previously (this vol., i, 190). Hypodermic injections of 0.028 g. per kg. body-weight (guinea-pig) produced no apparent distress (cf. Desgrez, *A.*, 1911, ii, 756). Buccal administration allowed of the use of greater concentrations, the toxic dose being found to be 0.75 g. per kg. body-weight. The symptoms produced resemble those obtained with hydrocyanic acid, post-mortem examination (six hours after administration of the toxic dose) revealing hypertrophy of the stomach, the volume of which is trebled, owing to the presence of fluid full of granules, but devoid of the tetrameride. Free hydrocyanic acid is present in the kidneys and, to a less extent, in the stomach.

Sodium thiosulphate, antidotal to hydrocyanic acid, does not react with the tetrameride, either in vitro or in vivo. If it is injected simultaneously with the tetrameride, the effects are modified. Death follows a single crisis, instead of several, and post-mortem examination shows a complete absence of hydrocyanic acid.

E. E. T.

## Chemistry of Vegetable Physiology and Agriculture.

**The Use of Calcium Carbonate in Nitrogen Fixation Experiments.** P. L. GAINNEY (*J. Agric. Res.*, 1923, 24, 185—190).—An inquiry is made as to the advisability of adding calcium carbonate to nutrient media for nitrogen fixation tests. A number of soils were examined and the organisms grown in media with and without calcium carbonate. The number of soils capable of initiating the growth of *Azotobacter* under experimental conditions was 20% greater when calcium carbonate was added to the media. The amount of nitrogen fixed in the presence of calcium carbonate was never less and was usually greater than in its absence. The beneficial effect of calcium carbonate was greater on other nitrogen-fixing organisms than on *Azotobacter* itself. A. G. P.

**Pyruvic Acid considered as an Anaërobiotic Factor.** ALBERT BERTHELOT (*Compt. rend.*, 1923, 176, 1929—1932; cf. A., 1921, i, 909).—*Bacillus aminophilus*, grown in peptonised dextrose solution, or in a synthetic mixture, causes the formation (among other reducing substances such as acetylmethylcarbinol) of pyruvic acid. When acetone-producing or acidaminolytic organisms are cultivated in a synthetic medium, where nitrogen is furnished by ammonium sulphate and potassium nitrate and carbon by an acyclic acid, pyruvic is the most readily utilised acid of the latter type (cf. Aubel, A., 1922, i, 201).

It is shown that the action of *B. aminophilus* and other favourable organisms is connected to a certain extent with the formation of pyruvic acid. Several strictly anaërobic bacilli were successfully cultivated in open tubes in presence of pyruvic acid, growth being more rapid after the formation of other reducing substances such as acetaldehyde or acetylmethylcarbinol. Under such conditions, pathogenic or saprophytic aerobic bacilli probably develop in addition. E. E. T.

**Production of Oxidising Ferments.** O. FERNÁNDEZ and T. GARMÉNDIA (*Anal. Fis. Quím.*, 1923, 21, 166—180).—A study of the effect of the commoner carbohydrates and amino-acids on the production of peroxylase and catalase by *Bacillus coli* under aerobic and anaerobic conditions. G. W. R.

**Production of  $\beta$ -Hydroxybutyric Acid by certain Bacteria of the Group *Bacillus subtilis*.** M. LEMOIGNE (*Compt. rend.*, 1923, 176, 1761—1763).—Macerations in sterile distilled water of certain microbes of the group *B. subtilis* rapidly become strongly acid. This acidity is due to the formation of  $\beta$ -hydroxybutyric acid, which was detected in the non-volatile residue by conversion into  $\alpha$ -crotonic acid, m. p. 70—71°, by distillation with sulphuric acid, and by the formation of acetone on oxidation with dichromate. G. F. M.

# ABSTRACTS OF CHEMICAL PAPERS.

**Antiseptic Action of Pyromucic Acid.** H. P. KAUFMANN (*Ber. Deut. pharm. Ges.*, 1923, 33, 132—139).—Pyromucic acid serves for inhibiting the growth of bacteria in pure cultures, but is useless for the preservation of fruit or meat. [Cf. *J.S.C.I.*, 1923.]  
T. H. P.

**The Problem of Aldehydes in Wines.** J. ESTALELLA (*Anal. Fis. Quím.*, 1923, 21, 33—44; cf. this vol., ii, 98; i, 181).—The author discusses the estimation of volatile acids and aldehydes in wines. The origin of aldehydes in wines is also discussed. These may be formed either as defensive secretions against added sulphites or else as intermediate stages in the formation of ethyl alcohol.  
G. W. R.

**Comparative Studies in Respiration. XXV. Action of Chloroform on the Oxidation of some Organic Acids.** GEORGE B. RAY (*J. Gen. Physiol.*, 1923, 5, 611—622).—When organic acids are treated with hydrogen and ferrous sulphate, carbon dioxide is evolved. Addition of an anæsthetic, e.g., chloroform, causes variation in the rate of production of the carbon dioxide. The curves showing the rate of production of carbon dioxide after addition of the anæsthetics resemble those obtained in a similar way using the alga *Ulva* instead of the acid (cf. this vol., i, 520). For example with tannic acid in presence of hydrogen peroxide and ferrous sulphate, the rate is initially decreased, then increased, and finally decreased again. Fumaric, maleic, oleic, and cinnamic acids—compounds containing a double bond—are all influenced by chloroform with regard to the rate at which carbon dioxide is produced.  
W. O. K.

**Comparative Studies on Respiration. XXVI. The Production of Carbon Dioxide from Organic Acids in Relation to their Iodine Absorption.** GEORGE B. RAY (*J. Gen. Physiol.*, 1923, 5, 623—627).—The effect of chloroform on the rate of adsorption of iodine by unsaturated acids runs very closely parallel to its effect on the rate of production of carbon dioxide under the influence of hydrogen peroxide and ferrous sulphate (cf. preceding abstract).  
W. O. K.

**The Composition of the Cell Sap of the Plant in Relation to the Adsorption of Ions.** D. R. HOAGLAND and A. R. DAVIS (*J. Gen. Physiol.*, 1923, 5, 629—646).—Measurements made of the composition and  $p_H$  of the cell sap of the fresh-water alga *Nitella* show that in the sap there is a much higher concentration of the inorganic ions than in the water in which the plants grow.  
W. O. K.

**The Glycerophosphatase of Plant Seeds. II.** ANTONÍN NĚMEC (*Biochem. Z.*, 1923, 138, 198—204).—A continuation of the author's previous work on the distribution and activity of glycerophosphatase in plant seeds (*A.*, 1920, i, 268, 354). The influence of acidity of seed extracts and reaction media is further

investigated. Five g. of each of a large number of fresh, finely powdered seeds are incubated for forty-eight hours with (1) 100 c.c. of water, (2) 100 c.c. of 1% sodium glycerophosphate, each in the presence of 2 c.c. of toluene, at  $p_H$  ranging from 4.65 to 7.3. The rate of hydrolysis of the glycerophosphate is measured by the difference of free  $P_2O_5$  in (2) and (1), and the activity of the enzyme is plotted against the  $p_H$  of the series of substrates. The optimum  $p_H$  is found to be 5.65. It is concluded that for a wide range of seeds the activity of glycerophosphatase is entirely a function of the  $p_H$  of the substrate, and not of varying amounts of enzyme.

J. P.

**Proteins of the Cantaloupe Seed, *Cucumis melo*. Isolation of a Crystalline Globulin [identical with] the Crystalline Globulin of the Squash Seed.** D. BREESE JONES and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1923, 56, 79—96).—By extraction with hot 2% sodium chloride solution, a crystalline globulin has been isolated from cantaloupe seeds. It crystallises in octahedra which have  $n_D^{20}$  1.545 approximately, has the elementary composition C=52.65, H=6.67, N=18.41, S=1.13%, and contains the following percentages of diamino-acids: arginine 16.26, histidine 4.22, lysine 3.29, cystine 1.27, tryptophan 2.63. It appears to be identical with the globulin isolated by Osborne (A., 1893, i, 380) from squash seed (*Cucurbita maxima*). A careful comparison of the globulins from the two sources has shown that they are identical in composition and in crystallographic and optical properties. Anaphylaxis experiments revealed no distinction immunologically.

When extracted with 0.5% sodium hydroxide, the residues from the extraction of the globulin yielded a glutelin with the elementary composition C=55.20, H=7.02, N=16.28, S=0.90%, and containing the following percentages of diamino-acids: arginine 12.42, histidine 2.72, lysine 4.59, cystine 1.09, tryptophan 3.03. The maximum yields of the proteins obtained were: globulin 12.07%, glutelin 5.78%. No albumin was detected in the seeds. E. S.

**Safflower Seed and its Germination.** V. A. TAMHANE (*Mem. Dept. Agric. India*, 1923, 6, 223—244).—The reserve materials in the safflower seed are chiefly oil and protein matter, no starch, glucosides, or tannin, and only a small proportion of a non-reducing sugar occurring in the resting seed. During germination, very little change occurs until the radicle protrudes from the seed, after which the oil rapidly disappears, a corresponding increase in the nitrogen-free extract occurs, due mainly to the formation of sugars. The lipase and oxydase rapidly increase as the radicle develops and reach a maximum when the lateral roots begin to appear, and at this stage the protein matter is largely solubilised. As the regular feeding roots are formed the proportion of enzymes gradually declines. It was observed that during germination the rise in the amount of oxydase follows somewhat the decomposition of the oil, but it is shown that the acidification of the oil during germination is not due to enzyme action.

G. F. M.

**Incrustive Substances of Plants. IV.** ERICH SCHMIDT and ALBERT MIERMEISTER (*Ber.*, 1923, 56, [B], 1438—1440).—The application of chlorine dioxide and sodium sulphite for the removal of incrustations from plants (cf. A., 1921, i, 912; 1922, i, 206; this vol., i, 274) is unsuitable for the *Alga*, the skeleton substance of which is dissolved by the alkali sulphite solution. In these cases, therefore, the latter reagent is replaced by alcohol.

The finely divided plant is washed, dried, powdered, and extracted with a mixture of alcohol and benzene (1:1) until the extract is colourless. Inorganic salts are removed by treatment with sulphuric acid (2%), after which the product is thoroughly washed with water. It is then subjected to the action of dilute chlorine dioxide solution (0.7%) in a closed vessel exposed to diffuse daylight during seventy-two hours. The residue is filtered, thoroughly agitated with water to remove excess of chlorine dioxide, repeatedly washed to eliminate hydrochloric acid, and extracted with boiling alcohol until the solvent is no longer coloured. The processes are repeated (about three times) until the removal of the incrustation is complete. The polysaccharides are obtained from the aqueous solutions derived from the first three treatments; the membrane components which are attacked by chlorine dioxide are isolated from the alcoholic extracts.

*Laminaria hyperborea* yields 19.5% of skeleton substance (ash 0.3%), 10.2% of polysaccharides (ash 20—22%) and 5% of attackable membrane, whereas *Fucus serratus* gives 26.8% of skeleton substances (ash 2.7%), 21.5% of polysaccharides (ash 20—25%), and 8.5% of attackable membrane. H. W.

**Nitrogen Reserve in Apple Trees.** R. H. ROBERTS (*Proc. Amer. Soc. Hort. Sci.*, 1921, 143—145; from *Physiol. Abstr.*, 1923, 8, 107).—Chemical analysis of branches of apple trees indicate that the carbohydrates decrease with an increase in nitrogen content, and increase with a decrease in nitrogen. Abundant blossom-bud formation occurred only on the trees which had an intermediate percentage of nitrogen and the reciprocal condition of an intermediate percentage of carbohydrate reserves.

W. O. K.

**The Behaviour of Bast Fibres under the Influence of Alkali Hydroxides.** C. R. NODDER and R. W. KINKEAD (*J. Text. Inst.*, 1923, 14, T133—156).—The percentage contraction produced by sodium hydroxide solutions of various concentrations in single fibres of flax and ramie and in yarns spun from these materials has been measured and the contraction-concentration curves are discussed, comparisons being made with the curves obtained by Willows and his colleagues for cotton (*ibid.*, 1922, 13, 229). The twisting phenomena exhibited by flax and ramie fibres during mercerisation have also been studied and the bearing of the results obtained on the production, of lustre on materials composed of bast fibres is indicated. The existence of certain relationships between the molecular composition of sodium hydroxide solutions and their action on vegetable fibres is discussed,

Coward and Spencer's data for cotton (this vol., i, 404) also being quoted. It is pointed out that the maximum contraction for bast fibres is with sodium hydroxide of  $d$  1.111, *i. e.*, a solution containing  $H_2O : NaOH$  in the ratio 20 : 1. This corresponds with one of the maxima for cotton. Another maximum for cotton is at  $d$  1.172, which corresponds with the maximum specific conductivity of sodium hydroxide solutions.

J. C. W.

**The Alleged Dextrin Reserves of Monocotyledons.** H. COLIN and H. BELVAL (*Compt. rend.*, 1923, 176, 1493—1495).—The water-soluble carbohydrate of *Hyacinthus orientalis* was examined and found to be a lævulosan, insoluble in alcohol, and yielding lævulose but not dextrose on hydrolysis. This appears to be characteristic of a number of monocotyledons, although starch is present in many cases, so that the views which have been put forward as to a carbohydrate reserve in the form of dextrins, and also as to the synthesis of starch from the latter, must be modified to some extent.

H. J. E.

**The Simultaneous Existence of both Optical Antipodes of Asparagine in the Germinating Lupin (*Lupinus albus*).** A. PRUTTI (*Bull. Soc. chim.*, 1923, [iv], 33, 804—806).—By prolonged boiling of an aqueous solution of 34 g. of *l*-asparagine, 0.545 g. of the *d*-isomeride was obtained, but it is possible to avoid this inversion by working at temperatures not exceeding 55°. The juice of the germinating lupin was expressed and the asparagine isolated as the copper salt. On removal of the copper by means of hydrogen sulphide (which has no inverting action on asparagine), a solution was obtained, which, on concentration in a vacuum at 40°, deposited crystals of both *d*- and *l*-asparagine. In a second experiment, the protein matter in the juice was precipitated by means of alcohol, and the asparagine obtained by crystallisation in a vacuum at 40°. Both isomerides were obtained as before. The small quantity of the *d*-form obtained points to the fact that this form is utilised by the plant in preference to the *l*-isomeride.

H. H.

**Composition of Maize Pollen. II. Concerning certain Lipoids, a Hydrocarbon, and Phytosterol Occurring in the Pollen of "White Flint" Maize.** R. J. ANDERSON (*J. Biol. Chem.*, 1923, 55, 611—628; cf. A., 1922, i, 508).—From alcoholic and ethereal extracts of the pollen the author has isolated a saturated hydrocarbon, m. p. 63.5—64°, which is apparently *n*-nonacosane; a saturated alcohol,  $C_{30}H_{62}O$ , m. p. 136°, isomeric with myricyl alcohol; and a phosphatide containing 4.09% of phosphorus. The substance, m. p. 88—89°, previously regarded as myricyl alcohol has now been identified as phytosterol palmitate. On hydrolysis, it yields palmitic acid and a mixture of phytosterols. The latter have been separated by fractional crystallisation into two fractions melting at 122° and 136.5°, respectively; the higher melting fraction gave an acetyl derivative, m. p. 101°. Other phytosterol preparations isolated from the pollen had melting points ranging from 121—154°. The preparation, m. p. 154°, gave an acetyl derivative,

m. p.  $134^{\circ}$ . All the phytosterol preparations differed from ordinary phytosterol in being optically inactive and in crystallising without water of crystallisation. E. S.

**Composition of *Nectandra coto*.** HARVEY A. SEIL (*J. Amer. Pharm. Assoc.*, 1922, **11**, 904—906).—The light petroleum extract (12.69%) of the bark of *Nectandra coto* contains most of the cotoin, whilst the ethyl-alcoholic extract (8.02%, after removal of 10.25% with ethyl ether) contains most of the tannin and alkaloids; the latter are present to the extent of 1.38%, of which 0.60% has phenolic properties. The non-phenolic alkaloid, *parostemine*, gives a crystalline precipitate with potassium mercuri-iodide reagent, and with a solution of iodine in aqueous potassium iodide. The phenolic alkaloid, *parosteminine*, gives a purplish-red colour with alcoholic ferric chloride. CHEMICAL ABSTRACTS.

**Hydrocyanic Acid in the Burma Bean (*Phaseolus lunatus*, sp.)** F. J. WARTH (*Mem. Dept. Agric. India*, 1923, **7**, 1—29).—For the estimation of hydrocyanic acid, auto-enzyme hydrolysis gives the best results, as when the organs, particularly the fresh leaves, are plunged into boiling water the glucoside is hydrolysed to a considerable extent, and part of the hydrocyanic acid is converted into a form which is not recoverable by acid hydrolysis. During sun-drying, hydrolysis occurs with evolution of hydrocyanic acid. Hydrolysis also occurs during slow drying, but auto-digestion of the hydrocyanic acid takes the place of evolution. Hydrocyanic acid has a powerful effect on cell permeability in the fresh leaf, and acts therefore as a regulator or hormone. Its presence brings glucoside hydrolysis to a premature end, and this paralysis of the enzyme plays an important part in regulating hydrocyanic acid liberation within the plant. In the green plant, the hydrolytic enzyme is active in the stalk, but the green pod and young ripe seed have no hydrolytic power. As the seed grows older, however, the enzyme develops. G. F. M.

**The Formation of Essential Oils in Conifers. I. The Process of Formation of the Essential Oil of *Pinus cembra*.** G. V. FIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 259—276).—The yield and nature of the essential oil from the needles and from the branches of several specimens of the Siberian cedar and from the branches of several specimens of the Siberian cedar (*Pinus cembra*, L.), grown near Petrograd, were investigated. It was found that the yield of oil varied from 0.42 to 1.49 c.c. per 100 g. of raw material. Old trees appear to give a smaller yield of oil; trees growing in the sun give more oil than those grown in the shade. The rotation of the different samples also presents very considerable differences, thus  $[\alpha]_D$  varies from  $-0.88^{\circ}$  to  $+22.96^{\circ}$ ; their dispersion from  $-19.8$  to  $1.83$ .

Fractionation of the oil shows that it is mainly composed of two constituents; the low-boiling portion consists of *d*-pinene (b. p.  $155.5$ — $156.5^{\circ}$ ,  $[\alpha]_D +36.84$ ,\*  $[\alpha]_t/[\alpha]_D$  1.94), the amount present varying from 65 to 78%; the high boiling portion consists of *l*-cadinene (b. p.  $135$ — $145^{\circ}/12$ — $15$  mm.,  $[\alpha]_D -67.52$ ,\*

\* These are the maximum rotations observed.

$[\alpha]_D/[\alpha]_L$  2.50). From these rotations and the rotations of the individual oils it is possible to calculate the percentage of the two constituents in them; the calculated values agree quite well with those arrived at by fractionating the samples; strongly dextrorotatory samples contain more *d*-pinene, and *vice versa*.

The oil obtained from the branches of *P. cembra* is laevorotatory,  $[\alpha]_D$   $-29.86^\circ$  to  $-47.76^\circ$ ,  $[\alpha]_L/[\alpha]_D$  1.77 to 2.15. The yield varies from 0.68 to 1.30% and is highest in trees which also give a high yield of needle-oil.  
G. A. R. K.

### The Formation of Essential Oils in Conifers. II. The Nature of the Essential Oil in Different Plant Organs.

(G. V. FIGULEVSKI (*J. Russ. Phys. Chem., Soc.* 1922, 54, 277—295).

—A comparison is made between the oils obtained from the needles and the branches of the following conifers: *Pinus silvestris* from the Crimea, *P. cembra* (Petrograd), *Abies sibirica* (Petrograd) and *Cupressus sempervirens* (Crimea).

For the first-named, it was found that the oil from the needles was feebly dextrorotatory  $[\alpha]_D +3.32^\circ$ ,  $d_4^{20}$  0.8692, whilst the oil from the twigs, etc., is laevorotatory,  $[\alpha]_D -10.12^\circ$  to  $-14.00^\circ$ ,  $d_4^{20}$  0.8659 to 0.8643; the oil derived from a whole tree shows intermediate properties. On fractionation, the needle oil gives about 40%, b. p. 157—160°,  $[\alpha]_D +7.24^\circ$ , and 21%, b. p. 160—161.5°,  $[\alpha]_D +5.88^\circ$ ; these fractions contain pinene which appears to be largely racemised; the high fraction is laevorotatory. When similarly treated the oil from the twigs gives about 61% of a fraction b. p. 162.5—168°,  $[\alpha]_D -7.23^\circ$ , also containing pinene together with a laevorotatory high fraction; the boiling point of the main portion of this oil is thus higher than that of the needle oil and the rotation of opposite sign.

The oil derived from the whole plant gives both these fractions, the lowest possessing a positive, the second a negative rotation. It may be mentioned that in all these experiments, the oxygen-containing constituents of the oils were destroyed by boiling with sodium.

The oil from the twigs of *P. cembra* (cf. preceding abstract) gives 80—84% of low fraction, b. p. 159—171°,  $[\alpha]_D -21.68$ — $-41.92^\circ$ , the residue showing a feeble laevorotation ( $-4.04^\circ$  to  $-6.52^\circ$ ) although it may contain a dextrorotatory constituent.

As in the case of *P. silvestris*, the oil prepared from twigs shows a higher boiling point and negative rotation.

The oil from the Siberian fir (*A. sibirica*) is characterised by its high content of esters (bornyl acetate). The oil derived from the needles has a rotation of about  $-46^\circ$  and a dispersion of 2.02 to 2.04. On fractionation, the hydrocarbon fraction obtained boils between 157° and 163° and has  $[\alpha]_D -54^\circ$  to  $-56^\circ$ ,  $[\alpha]_H/[\alpha]_D$  2.11; the ester content is about 48%. The oil derived from the twigs has a lower rotation ( $[\alpha]_D -30^\circ$  to  $-32^\circ$ ,  $[\alpha]_H/[\alpha]_D$  1.88 to 1.92). The hydrocarbon fraction has b. p. 163—170°,  $[\alpha]_D -39.20^\circ$ ,  $[\alpha]_H/[\alpha]_D$  1.98; the ester content is much lower, being only about 20%.

The properties of cypress oil have already been described (cf. this vol., i, 817); in this case again, the needle oil is dextrorotatory,

has a low coefficient of dispersion and a high ester content; the oil from the branches and stem is levorotatory, has a lower ester content and the hydrocarbon fraction has a higher boiling point.

The reasons leading to the differences in the character of the oils are discussed. It is suggested that in those parts of the plant in which the oxidative processes are most marked (e.g., the needles) the production of oxygen-containing compounds will be highest, and *vice versa*. It is well known that the presence of chlorophyll is connected with the same factor and it is suggested that the high ester content of Siberian fir-needle oil is due to the fact that the resinous ducts in this plant are situated in a region rich in chlorophyll, and, moreover, are not surrounded by a ring of bast fibres, as in *P. silvestris* and *P. cembra*.  
G. A. R. K.

**Availability of Potassium in Orthoclase for Plant Nutrition.** DENNIS EDWARD HALEY (*Soil. Sci.*, 1923, 15, 167—190).—The solubility of the potassium in orthoclase under varying conditions was determined by using the orthoclase as sole source of potassium in a series of sand cultures of buckwheat. A considerable amount of potassium could be extracted from a 200-mesh sample of orthoclase by water. The availability of potassium from orthoclase was sufficient for the growth of crops even larger than those obtained by the use of a complete nutrient solution. Calcium carbonate and sulphate tended to increase the amount of available potassium in orthoclase. Sodium sulphate made no appreciable difference to the availability of the potassium, and sodium chloride in most cases decreased it. When, however, the potassium supply became the limiting factor in the growth of the plant the addition of sodium chloride to orthoclase produced crop increases. The use of dextrose in the orthoclase mixture tended to lower the dry weight of plants produced. Similar results were obtained with starch, but in this case the addition of calcium carbonate brought about an increase in the dry weight of, and potassium absorbed by, the plants.  
A. G. P.

**Adsorption and Replacement of Plant Food in Colloidal Oxides of Iron and Aluminium.** D. C. LICHTENWALNER, A. L. FLENNER, and NEIL E. GORDON (*Soil Sci.*, 1923, 15, 157—165).—The adsorption of salts of calcium, potassium, and magnesium was studied by shaking standard solutions of the salts with iron and aluminium hydroxide gels and determining the quantities remaining in solution in the supernatant liquid. The order of adsorption of the cations was found to be calcium, magnesium, potassium, and of the anions phosphate, sulphate, nitrate. In the case of nitrates, adsorption was very slight. The time taken to reach equilibrium was considerably greater for phosphates than with other salts. The amount of adsorption of a particular salt increased with increased concentration. The adsorption of a cation depended to some extent on the particular anion with which it was associated. Phosphates replaced adsorbed sulphates, but the reverse change did not occur. Sulphates and nitrates adsorbed by hydrogels could be removed by washing, but about two-thirds of the adsorbed phosphate could not be leached out.  
A. G. P.

## Organic Chemistry.

**Preparation of Petroleum from Vegetable Oils.** A. MAILHE (*Compt. rend.*, 1923, 177, 202—204).—The yellow, strongly-smelling olefinic hydrocarbons (b. p. 240—280°) resulting from the pyrogenetic decomposition of vegetable oils (this vol., i, 88), on heating with anhydrous zinc chloride, are partly converted into viscous polymerisation products boiling above 330°, the portion (b. p. 240—280°) not polymerised now being colourless and odourless, but fluorescent.

Colza oil, on heating with a tenth of its weight of zinc chloride at 350—400°, is converted into water, acraldehyde, a gas, and a slightly acid liquid. The latter (the main product), after being washed with alkali, etc., has  $d^{18}_4$  0.8358, and on distillation affords the following fractions: (1) b. p. below 150°,  $d^{18}_4$  0.7202, analogous to American oil, (2) b. p. 150—240°,  $d^{18}_4$  0.7796, analogous to kerosene, (3) b. p. 240—280°, heavy oil,  $d^{18}_4$  0.8115, (4) b. p. 280—300°, heavy oil,  $d^{18}_4$  0.8358, (5) b. p. 300—320°, heavy oil,  $d^{18}_4$  0.8436, and (6) b. p. up to 400°. The entire product consists of paraffin and olefin hydrocarbons. Redistillation of the lower fraction shows the presence of hexane, hexylene, and two seven-carbon hydrocarbons.

The heavy oils boiling above 300° are partly polymerised when heated with zinc chloride, giving a yellow, fluorescent, viscous oil, b. p. 250—280°/37 mm.,  $d^{18}_4$  0.9004. Further polymerisation produces a solid, m. p. 40—42°. E. E. T.

**Preparation of Petroleum from Vegetable and Animal Oils.** ALPHONSE MAILHE (*Compt. rend.*, 1923, 177, 329—331).—Most of these oils, when heated with anhydrous zinc chloride, give products similar to those previously obtained from colza oil (preceding abstract). Rape-seed oil gives, after a single heating with 10% of its weight of zinc chloride, a mixture of paraffins and olefines, b. p. 60—310°, together with higher boiling substances (containing oxygen), which, on reheating with zinc chloride, afford a product resembling vaselin. Zinc chloride may be replaced, in these conversions, by anhydrous calcium, magnesium, barium, or sodium chlorides.

Karité butter, on heating with calcium chloride, affords an oil of  $d^{20}_4$  0.7158, b. p. mainly from 150—400°. When magnesium chloride is used, hydrogen chloride is evolved, but the product is similar. Whale oil and magnesium chloride give a liquid of approximately the same properties. E. E. T.

**The Relation between Low-temperature Tar, Coke-oven Tar, and Petroleum.** FRANZ FISCHER (*Ber.*, 1923, 56, [B], 1791—1794).—Low-temperature tar has been regarded by Fischer  
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as closely allied to natural petroleum, whereas Schütz has considered it to be closely related to coke-oven tar. Resemblances to petroleum are found in the optical activity of the hydrocarbons of low-temperature tar, the high hydrogen content of low-temperature tar, light oils, and the presence of solid paraffins (in place of anthracene). Benzene is only present in very small proportion (cf. Broche, this vol., i, 907); its presence in natural petroleum has been frequently observed. The occurrence of considerable proportions of carboic acid and of acetone in low-temperature tar has been observed solely by Schütz; it has not been confirmed in manufacturing practice by other workers.

H. W.

**Hydration of Hydrocarbons.** PAUL WOOG (*Compt. rend.*, 1923, 177, 60—62, 207—208).—By measuring the voltage required to produce a flow of current through an apparatus containing various saturated and unsaturated oily hydrocarbons (which are dry or moist in different experiments), the author concludes that unsaturated hydrocarbons have a greater affinity for water than saturated ones. The latter give up contained water more readily to the glass walls of the containing vessel.

If a saturated and an unsaturated oil are exposed, under the same conditions, to a moist atmosphere, the former soon becomes cloudy, whereas the latter remains transparent for a considerable time. If oils of the two types, and containing sufficient moisture to render them both cloudy, are warmed under similar conditions, the saturated oils clear first. This and the experiments above show that the hydration of saturated hydrocarbons is less stable than that of unsaturated ones.

When a drop of water on a glass rod is brought near to a bubble blown with the oils, a series of colour changes on the part of the oil film follows every movement of the water, the sensitiveness of this phenomenon being greater with unsaturated than with saturated hydrocarbons, owing to the action of the ethylenic linkings. The saturated molecules also, however, must possess points especially sensitive to the presence of water vapour.

E. E. T.

**A Saturated Hydrocarbon from Shark Liver Oils.** YOSHIYUKI TOYAMA (*Chem. Umschau*, 1923, 30, 181—187).—The hydrocarbon isooctadecane ( $C_{18}H_{38}$ ) previously isolated by Tsujimoto from one sample of the liver oil of the giant shark was isolated from the liver oils of a number of species of shark and appears to be a general constituent of various liver oils containing squalene. The pure hydrocarbon, which is named *pristane*, has the following characters:  $n_D^{20}$  1.4410,  $n_D^{25}$  1.4390;  $d_4^{20}$  0.7871,  $d_4^{25}$  0.7835; b. p. 158°/10 mm., 169°/15 mm., 187°/30 mm., 220°/100 mm., 296°/760 mm., without decomposition. Absolute viscosity at 30°, 0.443. It is optically inactive.

H. C. R.

**Action of Selenium Oxychloride on Ethylene, Propylene, Butylene, and Amylene.** CARL E. FRICK (*J. Amer. Chem. Soc.*, 1923, 45, 1795—1800).—When selenium oxychloride reacts with the olefines, the dichlorides of the corresponding alkyl selenides are formed, regardless of whether the olefine or the selenium oxy-

chloride is in excess. Thus the product from ethylene and selenium oxychloride is di- $\beta$ -chloroethylselenium dichloride, whilst di- $\beta$ -chloropropylselenium dichloride is formed when propylene is used; di- $\beta$ -chlorobutylselenium dichloride, from  $\beta$ -butylene, and di- $\beta$ -chloroamylselenium dichloride, from amylene, although probably formed when the reaction is conducted at temperatures below  $10^{\circ}$ , were not isolated in a pure condition. This reaction, which is formulated:  $2C_nH_{2n} + 2Cl_2SeO = (ClC_nH_{2n})_2SeCl_2 + SeO_2$ , leads, therefore, to the same products as the action of excess of selenium monochloride on olefines (Boord and Cope, A., 1922, i, 421),  $2C_nH_{2n} + 2Cl_2Se : Se = (ClC_nH_{2n})_2SeCl_2 + 3Se$ ; it is held that these results confirm the unsymmetrical formula,  $Se:SeCl_2$ , for selenium monochloride. W. S. N.

**Catalytic Hydrogenation and Steric Hindrance.** G. VAVON and S. KLEINER (*Compt. rend.*, 1923, 177, 401–403; cf. this vol., i, 464).—A study of the relative extents of hydrogenation of (a)  $\Delta^7$ -heptene, (b)  $\beta\delta$ -dimethyl- $\Delta^5$ -pentene, (c)  $\gamma$ -ethyl- $\Delta^5$ -pentene, and (d)  $\beta$ -methyl- $\Delta^5$ -pentene. The olefine (1 mol.) to be examined was mixed with either  $\alpha$ -pinene or undecenoic acid (1 mol.) in presence of an inert solvent (cyclohexane or pinane), and the mixture allowed to combine with 1 mol. of hydrogen, in presence of platinum black. The amount of hydrogen appropriated by the olefine was determined polarimetrically in the case of pinene mixtures, and by extraction with alkali, followed by bromine titrations of each layer in the case of mixtures with the acid. Olefines b and c reduce to about the same extent, which is greater than that for d and less than that for a.

Similar experiments on the addition of bromine (in presence of undecenoic acid) to the olefines indicated that the four substances in question combine with bromine in the (decreasing) order: d, b, c, a. These results, unlike those with hydrogen, do not fall into line with the theory of steric hindrance. E. E. T.

**A Method for the Bromination of Organic Substances.** ERICH KRAUSE (*Ber.*, 1923, 56, [B], 1801).—The method described recently by Rosenmund and Kuhnheim (this vol., i, 782) has been used previously by the author (A., 1918, i, 415). H. W.

**Specific Gravity of Absolute Ethyl Alcohol at  $20^{\circ}$ .** C. N. RÜBER (*Z. Elektrochem.*, 1923, 29, 334–338).—Absolute ethyl alcohol, purified by boiling with calcium ethoxide and repeated fractionation in a current of hydrogen, has been used for the determination of its specific gravity. As the mean of three values which differ only in the seventh place of decimals, the value  $d_{20}^{20}$   $0.789334 \pm 0.000003$  is obtained, using the value  $d_{20}^{20}$   $0.998232$  for water. The figure given refers to ethyl alcohol saturated with dry air at  $20^{\circ}$ . J. F. S.

**New Method of Passing from Mesityl Oxide to Tetramethylglycerol [ $\beta\delta$ -Dimethylpentane- $\beta\gamma\delta$ -triol].** PASTUREAU and H. BERNARD (*Compt. rend.*, 1923, 177, 327–329; cf. A., 1922, i, 717; this vol., i, 646).—Magnesium methyl iodide converts

mesityl oxide into  $\beta\beta$ -dimethyl- $\Delta^5$ -pentene-3-ol (cf. von Fellenberg, A., 1904, i, 961), which, with hypiodous acid, affords the iodohydrin of tetramethylglycerol. This substance, when heated with powdered potassium hydroxide, gives the corresponding glycide, whilst silver acetate affords the acetin (m. p.  $87^\circ$ ). The glycide is converted into tetramethylglycerol by evaporating its aqueous solution.

The pentenol (above) cannot be oxidised, using permanganate, to give the glycerol, both this substance and the pentenol being oxidised to give acetone, formaldehyde, and formic acid. In the case of the glycerol, this oxidation is even effected by oxygen in presence of ferrous sulphate solution.

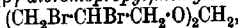
Hypochlorous acid converts the pentenol, not into the expected chlorohydrin, but into a crystalline substance of unknown constitution.

E. E. T.

**Oxonium Compounds in the Vapour State. Methyl Ether-Hydrogen Chloride.** O. MAASS and D. M. MORRISON (*J. Amer. Chem. Soc.*, 1923, 45, 1675—1682).—Equal volumes of methyl ether and hydrogen chloride were mixed in the gaseous state at atmospheric pressure and the resultant pressures of the mixture were recorded over the temperature range  $30^\circ$  to  $-10^\circ$ . From these data the amount associated to form the oxonium compound,  $\text{OHMe}_2\text{Cl}$ , has been calculated, and the resultant pressures on mixing these gases at pressures other than atmospheric and in unequal proportions were deduced. These latter have been checked experimentally, thus proving the original assumption to be correct, namely, that an equimolecular compound between methyl ether and hydrogen chloride exists in the vapour state, the dissociation of which increases with rising temperature. The similarity between methyl ether-hydrogen chloride and ammonium chloride has been pointed out, and the formation of the first-named compound is attributed to induced polarity in the methyl ether molecule caused by the polar hydrogen chloride molecule.

J. F. S.

**Dipropargyl Methylene Ether.** HERBERT H. GUEST (*J. Amer. Chem. Soc.*, 1923, 45, 1804—1807).—Dibromohydrin and paraformaldehyde react in the cold in the presence of dry hydrogen chloride, or at  $125$ — $150^\circ$  in the presence of anhydrous ferric chloride, giving *di*-( $\beta$ -dibromopropyl)methylene ether,



b. p.  $220^\circ/7$  mm., which is converted, by the action of a slight excess of finely powdered potassium hydroxide on its cold ethereal solution, into *di*-( $\beta$ -bromoalkyl)methylene ether,  $(\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2$ , b. p.  $135$ — $140^\circ/10$  mm. If, however, boiling aqueous alcoholic potassium hydroxide is used, the product is *dipropargylmethylene ether*,  $(\text{CH}_2\text{C}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2$ , b. p.  $75$ — $80^\circ/10$  mm., or  $162^\circ/760$  mm. This forms an explosive silver salt, but the silver atom is non-reactive towards alkyl halides. Dipropargylmethylene ether reacts with magnesium ethyl bromide in cold ethereal solution with evolution of ethane, but a pure product has not been isolated.

W. S. N.

**Preparation of Esters and Ethers of Ethyldene Glycol and Vinyl Alcohol.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Brit. Pat. 182112).—A mixture of acetylene and the vapours of a substance containing a hydroxyl or carboxyl group is passed over a heated catalyst, metals, and their oxides and salts, being especially effective [cf. *J.S.C.I.*, 1923, 42, 861A]. W. T. K. B.

**Esters of Chromic Acid. II. Esters of Chromic Acid with Alcohols of the Aliphatic and Aromatic Series.** HEINRICH WIENHAUS and WILHELM TREIBS (*Ber.*, 1923, 56, [B], 1648—1653).—The esters indicated in the title cannot be prepared as in the case of terpene and sesquiterpene alcohols by agitating the alcohols with aqueous chromic acid solution. It is generally necessary to treat the solution of the alcohol in light petroleum, carbon tetrachloride, carbon disulphide, or benzene with solid chromium trioxide. The action of organic halides on silver chromate is fairly generally applicable.

Unstable chromates are produced by the action of chromium trioxide on methyl, ethyl, or isopropyl alcohol dissolved in much light petroleum or carbon tetrachloride; cetyl and melissyl chromates appear to be rather more stable. The results point to the possibility of isolating the esters at a sufficiently low temperature. *Trimethylcarbinyl chromate*,  $(C_4H_9)_3CrO_4$ , is obtained as an unstable, viscous, red liquid by the action of chromium trioxide on trimethylcarbinol in the presence of light petroleum or from chlorotrimethylmethane and silver chromate in the presence of ether or light petroleum. *Dimethylethylcarbinyl chromate* is prepared in a similar manner. *Dimethylpentadecylcarbinol*, m. p. 34–35°, dissolved in light petroleum, is converted by chromium trioxide into *dimethylpentadecyl chromate*, a yellowish-red, wax-like mass; it is very stable, although decomposing readily on exposure to light. *Linalyl*, *dihydrolinalyl*, and *tetrahydrolinalyl chromates* are red liquids.

The presence of a phenyl group generally renders the chromates unstable. If, however, the solubility of the product in dissociating media is depressed by the presence of a relatively large, aliphatic radicle, chromates containing the phenyl group can be readily prepared in a state of purity; they are stable. *Phenylmethylethylcarbinyl chromate* is highly unstable; *diphenylmethylethylcarbinyl chromate*, a red oil which does not solidify, is considerably more stable. *Diphenylpentadecylcarbinyl chromate* is a viscous, red liquid which is stable except towards light. *Triphenylcarbinyl chromate*, prepared from triphenylcarbinol and chromium trioxide in the presence of benzene or carbon tetrachloride, forms red crystals.

H. W.

**Mixed Organic Sulphides and Cyanogen Bromide.** JULIUS VON BRAUN and PAUL ENGELBERTZ (*Ber.*, 1923, 56, [B], 1573—1577).—The action of cyanogen bromide on mixed organic sulphides containing purely aliphatic radicles results in the exclusive elimination of the smaller group as alkyl bromide. The benzyl radicle is more readily lost than the smallest aliphatic group. With benzyl allyl sulphide, both groups are removed from the sulphur

atom, but the extent is much greater with the benzyl complex. An almost complete parallelism exists between sulphur and nitrogen with regard to the relative firmness with which the separate organic radicles are attacked. With arsenic, the parallelism is not quite so close, doubtless owing to the more metallic nature of the element.

Ammonium dithiocarbamate is gradually transformed by *n*-butyl bromide in the presence of alcohol into *n*-butyldithiourethane,  $C_4H_{11}NS_2$ , m. p. 46–47°, which is converted by dilute potassium hydroxide solution into *n*-butyl mercaptan, b. p. 99–100°, the yield being 70% of that theoretically possible.

*n*-Propyl *n*-butyl sulphide, a colourless, mobile liquid, b. p. 153–155°, is converted by cyanogen bromide at 60–70° into *n*-propyl bromide and *n*-butyl thiocyanate, b. p. 173–175°. Ethyl propyl sulphide gives ethyl bromide and propyl thiocyanate, b. p. 161–163°, whereas methyl ethyl sulphide yields methyl bromide and ethyl thiocyanate, b. p. 140–141°. Benzyl methyl sulphide is transformed into benzyl bromide and methyl thiocyanate, b. p. 130–132°, whereas benzyl allyl sulphide, b. p. 121–122°/12 mm., is converted to a small extent into allyl bromide and benzyl thiocyanate, but mainly into benzyl bromide and allyl thiocyanate.

H. W.

**A New Preparation of Monochloroacetic Acid.** L. J. SIMON and G. CHAVANNE (*Bull. Soc. chim. Belg.*, 1923, 32, 285–287).—A republication of work previously described (this vol., i, 177). As sulphuric acid of definite concentration must be used, the following reaction mechanism is suggested: (1) addition of sulphuric acid as with ethylene,  $CH_2ClCCl_2 + H_2SO_4 \rightarrow CH_2ClCCl_2 \cdot O \cdot SO_3H$ , (2) hydrolysis of the resulting sulphonic acid,  $CH_2ClCCl_2 \cdot O \cdot SO_3H + H_2O \rightarrow CH_2ClCCl_2 \cdot OH + H_2SO_4$ , and  $CH_2ClCCl_2 \cdot OH \rightarrow CH_2ClCOCl + HCl$ , (3) reaction with water of the acid chloride so formed,  $CH_2ClCOCl + H_2O \rightarrow CH_2ClCO_2H + HCl$ .

The use of fuming sulphuric acid (cf. Böseken, A., 1913, i, 330) with subsequent dilution results in a much reduced yield.

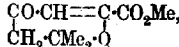
H. J. E.

**Heptadecic Acid.** A. HEIDUSCHKA and J. RIPPER (*Ber.*, 1923, 56, [B], 1736–1739).—An intimate mixture of silver stearate, iodine, and fragments of porcelain is heated at 130–140°, whereby heptadecyl stearate,  $C_{17}H_{35} \cdot CO_2C_{17}H_{35}$ , small leaflets, m. p. 64–65°, is obtained; this is hydrolysed by boiling alcoholic potassium hydroxide solution to heptadecyl alcohol, leaflets, m. p. 54°, the yield being 55%. The alcohol is converted into heptadecic acid,  $C_{17}H_{33} \cdot CO_2H$ , microscopic rhombs, m. p. 59–9°, by treatment with molten potassium hydroxide in an open vessel at 240–250°. Lead, silver, and copper heptadecoates are described.

H. W.

**The X-Ray Investigation of Fatty Acids.** ALEX. MÜLLER (*T.*, 1923, 123, 2043–2047).

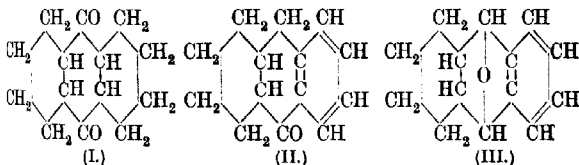
The Spectrochemical Behaviour and the Constitution of Methyl  $\beta$ -Mesityloxydeoxalate [Methyl 2:2-Dimethyl-2:3-dihydro-4-pyrone-6-carboxylate]. K. VON AUWERS and W. DIECKMANN (*Ber.*, 1923, 56, [B], 1527—1530).—Previous refractometric measurements with this compound have afforded evidence in favour of the closed ring formula,



rather than the open-chain formula,  $\text{CMe}_2\text{:CH-CO-CH}_2\text{-CO-CO}_2\text{Me}$ . These measurements, however, were made in chloroform solution, on account of the high melting point of the compound. New measurements have been made with the ester in the fused state at 85.9° and have confirmed the older view that the ester contains the group  $-\text{CO-C(CO)-CO}-$ , and must therefore possess the cyclic structure. This view is supported by measurements made with the ethyl ether of ethyl acetoneoxalate,  $\text{COMe-CH:C(OEt)-CO}_2\text{Et}$ . The following figures are quoted. Methyl  $\beta$ -mesityloxydeoxalate,  $d_4^{20}$  1.0933,  $d_4^{25}$  1.0920,  $n_D$  1.46398,  $n_D$  1.45814 [? 1.46814],  $n_D$  1.47959 at 85.9°; ethyl ether of ethyl acetoneoxalate, b. p. 131°/14 mm., 123—129°/10 mm.,  $d_4^{15.5}$  1.0661,  $d_4^{15.5}$  1.0644,  $d_4^{20}$  1.061, 1.060,  $n_D$  1.46773,  $n_D$  1.47212,  $n_D$  1.48437 at 14.05°,  $n_D$  1.46655,  $n_D$  1.47103,  $n_D$  1.48316,  $n_D$  1.49452 at 15.3°,  $n_D^{20}$  1.4694, 1.4689. H. H.

#### Thermal Decomposition of some Dicarboxylic Acids.

A. WINDAUS and M. EHRENSTEIN (*Nachr. K. Ges. Wiss. Göttingen*, 1922, 1—7; from *Chem. Zentr.*, 1923, i, 831; cf. Windaus and Hückel, A., 1922, i, 658).—Barium  $\beta\beta$ -dimethylglutarate by dry distillation gives, in addition to unidentified products, acetone, mesityl oxide, and isophorone. Dimethylcyclobutanone, although not found, was probably formed as an intermediate stage, giving mesityl oxide by rearrangement. Acetone was probably formed by hydrolytic decomposition of mesityl oxide, and isophorone by condensation of acetone, or of acetone with mesityl oxide. *cis*-Hexahydrophthalic anhydride gives off carbon dioxide at about 380°, a dodecahydroanthraquinone (I) being probably first formed, which loses hydrogen by which the keto-groups are reduced. A certain amount of anthraquinone was found as well as a compound,  $\text{C}_{14}\text{H}_{16}\text{O}$ , which was probably an anthracene derivative (II or III). It is a yellowish-brown, slightly fluorescent oil, forming



white platelets, m. p. 97—98°. A mixture of hydrogenated anthracenes was also obtained in which the hydrocarbons  $\text{C}_{14}\text{H}_{20}$  and  $\text{C}_{14}\text{H}_{22}$  predominated. Hexahydro-*o*-phthalic acid is obtained by catalytic hydrogenation of tetrahydro-*o*-phthalic acid.

G. W. R.

**Resolution of the  $\alpha\delta$ -Dihydroxy- $\alpha$ -methyl- $\delta$ -isopropyladipic Acids.** THOMAS ANDERSON HENRY and HUMPHREY PAGET (T., 1923, 123, 1878—1887).

**Dihydroxymaleic Acid (Dihydroxyfumaric Acid).** J. BÖSEKEN and J. I. DE VOOGD (*Rec. trav. chim.*, 1923, 42, 745—749).—The authors have prepared dihydroxymaleic and dihydroxyfumaric acids by a method which is a slight modification of that of Fenton (T., 1894, 65, 899) and have investigated these two substances by means of electrical conductivity and refractive index measurements, and conclude that these two acids are both dihydroxymaleic acids. J. F. S.

**Citrates of Calcium and Strontium.** K. P. CHATTERJEE (*J. Proc. Asiatic Soc. Bengal; Proc. Eighth Indian Sci. Cong.*, 1921, 17, cxxix—cxxx).—The gelatinous, hygroscopic compound  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 16\text{H}_2\text{O}$  is precipitated when strong solutions of sodium citrate and calcium chloride are mixed. It passes rapidly into the hexahydrate, which separates in the cold with increasing rapidity up to  $70^\circ$ ; above this temperature, the tetrahydrate separates, its solubility decreasing with temperature. On being warmed, the hexahydrate yields the tetrahydrate, the compound  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 1.5\text{H}_2\text{O}$  being obtained at  $110^\circ$ . Gelatinous strontium citrate, and a penta- and a mono-hydrate, having analogous properties, have been obtained. CHEMICAL ABSTRACTS.

**Preparation of Glyoxal and Glyoxal Sulphate.** CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (KARL OTT) (D.R.P. 362743; from *Chem. Zentr.*, 1923, ii, 743).—Tetrahalogenoethanes are treated with fuming sulphuric acid with or without addition of heavy metals, and glyoxal is obtained from the sulphate thus formed. For example, tetrachloroethane with mercuric sulphate or copper sulphate in suspension is added to fuming sulphuric acid containing 65% of sulphur trioxide. *Glyoxal sulphate*, which separates on cooling, forms colourless needles, m. p.  $176$ — $177^\circ$ . The reaction whereby it is formed is probably  $\text{C}_2\text{H}_2\text{Cl}_4 + 4\text{SO}_3 + 2\text{H}_2\text{SO}_4 = 4\text{SO}_3\text{HCl} + \text{SO}_2 < \overset{\text{O}}{\underset{\text{O}}{\text{C}}} > \text{CH} \cdot \text{CH} < \overset{\text{O}}{\underset{\text{O}}{\text{C}}} > \text{SO}_2$ . Glyoxal is obtained by heating the sulphate with water. G. W. R.

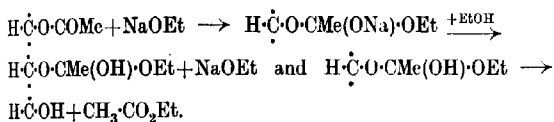
**Condensing Action of Mixed Magnesium Alkylloxides,  $\text{RO} \cdot \text{Mg} \cdot \text{X}$ .** V. GRIGNARD and M. DUBIEN (*Compt. rend.*, 1923, 177, 299—302).—The condensation of ketones, which sometimes occurs during their interaction with Grignard reagents (cf. this vol., i, 739), has been traced to the condensing action of compounds of the type  $\text{RO} \cdot \text{Mg} \cdot \text{X}$ , produced during such reactions. Thus *n*-butaldehyde is rapidly converted, in presence of an ethereal suspension of magnesium ethoxydide, into  $\beta$ -hydroxy- $\alpha$ -ethyl-*n*-hexanal,  $\text{CH}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHEt} \cdot \text{CHO}$  (colourless liquid, b. p.  $103$ — $105^\circ/14$  mm., polymerising readily and giving a semicarbazone, m. p.  $147^\circ$ ), small quantities of *n*-butyl and ethyl butyrates being formed in addition,

Magnesium ethoxyiodide causes the partial conversion of acetone into diacetone alcohol (cf. Locquin, this vol., i, 440).

The magnesium derivative formed by the addition of magnesium methyl iodide to *n*-butylideneacetone causes the condensation of the latter substance to give a carbinol, which undergoes loss of the elements of water on distillation. (The product was therefore heated with a little iodine, to complete this loss of water.) In this way, dibutylideneacetone was isolated. E. E. T.

**The Sodium Compound of Dextrose and the Hydrolysis of Acylated Sugars.** GÉZA ZEMPLÉN and ALFONS KUNZ (*Ber.*, 1923, 56, [B], 1705—1710).—A sodium compound of dextrose has been described frequently in the literature and has generally been regarded as a substituted alkoxide. It does not, however, react in the manner characteristic of this class of compounds. Investigation of it has shown that it is an additive compound of molecular proportions of dextrose and sodium ethoxide.

When dextrose penta-acetate is treated with a cold, absolute alcoholic solution of sodium ethoxide, a sodium derivative speedily separates which yields ethyl acetate when treated with water. The formation of this intermediate compound gives the clue to the mechanism of the hydrolysis of acetylated sugars by sodium ethoxide, for which, as noted previously by Fischer and Bergmann, considerably less ethoxide is required than is necessary according to theory with the acetyl groups which are present. The reaction is represented by the scheme :



The action of sodium ethoxide on acetobromoglucose in absolute alcoholic solution has also been examined. A precipitate similar to that obtained from dextrose penta-acetate is formed in small amount, but the bulk of the dextrose remains in solution and is converted into  $\beta$ -ethylglucoside; this is shown by its transformation into  $\beta$ -ethylglucoside tetra-acetate. The by-products of the change appear to be much more complex than those derived from the penta-acetate. H. W.

**Fermentative Hydrolysis of  $\beta$ -Alkyl Glucosides. Indices for Emulsin. Estimation of Molecular Weights.** H. COLIN and (MLLE) A. CHAUDUN (*Bull. Soc. Chim. biol.*, 1923, 5, 382—388).—The method previously described (A., 1921, ii, 225) for estimating the molecular weights of certain polysaccharoses has been extended to the estimation of the molecular weights of  $\beta$ -alkyl glucosides. The method depends on the fact that the amount of glucoside fixed by a given quantity of emulsin is proportional to its molecular weight. E. S.

**Action of Ferments on Sulphuric and Phosphoric Acid Esters of Sugars and their Derivatives.** BURCKHARDT HELFERICH, ALBRECHT LÖWA, WALDEMAR NIPPE, and HANS RIEDEL (*Z. physiol. Chem.*, 1923, 128, 141—153).—By the action of sulphuryl chloride or of phosphoryl chloride on various sugar derivatives, the corresponding esters have been obtained and isolated as their barium salts as follows. *Barium  $\alpha$ -methylglucoside sulphate*,  $[\alpha]_D^{25} + 81.16^\circ$ . *Barium  $\beta$ -methylglucoside sulphate*,  $[\alpha]_D^{25} - 19.12^\circ$ . *Barium methylmaltoide sulphate*,  $[\alpha]_D^{25} + 53.8^\circ$ . *Barium trehalose sulphate*,  $[\alpha]_D^{25} + 128.75^\circ$ . *Barium amygdalic acid sulphate*,  $[\alpha]_D^{25} - 45.1^\circ$ . *Barium methylcelloside sulphate*,  $[\alpha]_D^{25} - 16.2^\circ$ . *Barium  $\beta$ -methylglucoside phosphate*,  $[\alpha]_D^{25} - 31.0^\circ$ . *Barium  $\beta$ -phenylglucoside phosphate*,  $[\alpha]_D^{25} - 51.1^\circ$ . *Barium trehalose phosphate*,  $[\alpha]_D^{25} + 135.5^\circ$ . *Barium methylcelloside phosphate*,  $[\alpha]_D^{25} - 14.98^\circ$ . *Barium amygdalic acid phosphate*,  $[\alpha]_D^{25} - 49.0^\circ$ . All the rotations are measured in aqueous solution. Hepta-acetylmethylcelloside, m. p.  $186.5^\circ$ ,  $[\alpha]_D^{25} - 26.03^\circ$  in tetrachloroethane,  $[\alpha]_D^{25} - 31.61^\circ$  in acetic acid, is obtained from acetobromocellose and methyl alcohol in presence of silver oxide. When hydrolysed with methyl-alcoholic ammonia, it yields *methylcelloside*, bevelled prisms, m. p.  $193^\circ$ ,  $[\alpha]_D^{25} - 18.69^\circ$  in water. The action of  $\alpha$ - and  $\beta$ -glucosidases on these esters has been investigated, but in every case they have been found inactive.

W. O. K.

**Preparation of Rare Sugars [Arabinose, Rhamnose, Xylose, Galactose, Melezitose, Raffinose, and Maltose].** T. SWANN HARDING (*Sugar*, 1922, 406; 1923, 82—83, 124—125, 175—176, 240—241, 308—310, 350—352).—*Arabinose*: 300 g. of beet pulp are hydrolysed by boiling for one and a half hours with 6 litres of 1% sulphuric acid, neutralised with 175 g. of barium hydroxide, and allowed to subside; the supernatant liquid is clarified with basic lead acetate, the excess removed as sulphide, decolorising carbon added, and the whole filtered; after concentration to about  $\frac{1}{4}$  litre, 500 c.c. of 95% alcohol are added for the elimination of organic acids, colouring matter, and salts, and crystallisation is effected from alcoholic solution containing 1% of nitric acid, the yield being 4—5% of the weight of raw material. *Rhamnose*: black oak bark is boiled with water, and the extract concentrated for the crystallisation of the quercitrin, which glucoside is hydrolysed with 0.4% sulphuric acid; the resulting liquid is filtered, clarified with basic lead acetate, decoloured, and evaporated to a syrup of about 80% solids, which readily crystallises, the yield being about 1% of the raw material. *Xylose*: 1 kg. of corn cobs is boiled for two hours with 6 litres of 4% sulphuric acid, and the liquid is filtered, neutralised with barium carbonate, filtered, and evaporated to a thick syrup, from which the sugar crystallises by the addition of alcohol, the yield being about 12%. *Galactose*: Clark's method (*A.*, 1921, i, 647) is preferred, the yield in the author's hands being 35—37%. *Melezitose*: honey collected from the Douglas fir is dissolved in water, the extract cooled, and the wax separated; after clarifying with kieselguhr and decolorising

carbon, and concentrating, the trisaccharide crystallises out, the yield on recrystallisation being about 22%. *Raffinose*: 6 kg. of cotton-seed meal are extracted with 30 litres of water containing 750 g. of aluminium sulphate, filtered, and evaporated to 3 litres, to which are added 6 litres of 80% alcohol; after subsiding, the liquid is clarified with basic lead acetate, filtered, delead, treated with decolorising carbon, and filtered; the alcohol is eliminated, and the residue concentrated to 300 c.c., from which syrup after adding 95% alcohol the sugar will crystallise out on keeping, the yield thus obtained being about 2%. *Maltose*: soluble starch is saccharified with barley flour, the resulting dextrins being very much less soluble in alcohol than when malt extract is used. Previous work on the elaboration of methods for the preparation of these sugars is summarised.

J. P. O.

**System Sucrose-Sodium Chloride-Water and the Combination of these Constituents.** N. SCHOORL (*Rec. trav. chim.*, 1923, 42, 790—799).—A method is described which allows the existence of one or more compounds of two components being established. The method consists in the determination of the vapour pressure of the saturated solution of various mixtures of the two solid components. If the curve shows an *euhygroscopic* point, or if there is a special branch in the curve, then the existence of a compound is indicated. The term *euhygroscopic* denotes a point of minimum vapour pressure, and is analogous to the term eutectic. Vapour-pressure curves and solubility curves of mixtures of sucrose and sodium chloride have been determined at 25°, and it is shown that an equimolecular compound, crystallised with 2 molecules of water,  $C_{12}H_{22}O_{11} \cdot NaCl \cdot 2H_2O$ , exists.

J. F. S.

**Starch. VIII. The Characterisation of the Polyamyloses.** HANS PRINGSHEIM and KURT GOLDSTEIN (*Ber.*, 1923, 56, [B], 1520—1526).—The authors' conception that  $\beta$ -hexa-amylose is a dimeric tri-amylose and  $\alpha$ -hexa-amylose is a trimeric diamylose has not met with universal acceptance. It is, however, strengthened by the observations that the molecular weight of methylated  $\beta$ -hexa-amylose in benzene solution agrees with the theoretical value, whereas that of methylated tri-amylose is somewhat high in benzene but normal in phenol. The molecular weight of methylated  $\alpha$ -hexa-amylose confirms its conception as a trimeric diamylose.

$\beta$ -Hexa-amylose is converted by methyl sulphate and potassium hydroxide solution or by this mixture followed by silver oxide and methyl iodide into *dodecamethyl- $\beta$ -hexa-amylose*,  $(C_6H_8O_5Me_2)_6$ ,  $[\alpha]_D^{20} +143.20^\circ$  in ethyl-alcoholic solution; attempts to methylate the product further were not generally successful, although in one instance a more highly methylated product was obtained. Methylation of triamylose gives *hexamethyltriamylose*,  $(C_6H_8O_5Me_2)_3$ , hexagonal plates,  $[\alpha]_D^{20} +138.38^\circ$  in ethyl-alcoholic solution. *Dodecamethyl- $\alpha$ -hexa-amylose* crystallises in well-defined rhombohedra,  $[\alpha]_D^{20} +148.73^\circ$  when dissolved in ethyl alcohol.

$\beta$ -Hexa-amylose and  $\alpha$ -tetra-amylose are converted by phos-

phoryl chloride in the presence of pyridine at  $-15^{\circ}$  into *phosphoric esters*, which appear to contain one phosphoric acid residue for each dextrose residue; for some unexplained reason, the carbon content of these compounds is considerably lower than that demanded by theory.

The benzylation of the polyamyloses has been investigated further (cf. Pringsheim and Eissler, A., 1913, i, 1156; Karrer, A., 1922, i, 1119). Tetra-amylose is converted by benzoyl chloride and sodium hydroxide solution (1%) at  $-2^{\circ}$  into dibenzoyldiamylose, whereas in the presence of more concentrated sodium hydroxide solution at the atmospheric temperature it is transformed into tetrabenzoyldiamylose. Under similar conditions,  $\beta$ -hexa-amylose yields tribenzoyltriamylose and hexabenzoyltriamylose. H. W.

**The Action of Concentrated Hydrochloric Acid on Different Celluloses.** E. C. SHERRARD and A. W. FROEHLKE (*J. Amer. Chem. Soc.*, 1923, **45**, 1729—1734).—The hydrolysis of celluloses from cotton, white spruce, Douglas fir, and yellow birch, by means of 41% hydrochloric acid at  $20^{\circ}$ , has been followed by measuring the specific rotation, and by estimating the reducing sugars by means of Fehling's solution, the results being shown graphically. The specific rotation curves for cotton and white spruce cellulose are practically identical, although the latter contains mannose, but Douglas fir cellulose, and more particularly yellow birch cellulose, are hydrolysed more rapidly; since yellow birch contains about 28% of pentosan, this is not surprising. Each curve shows two breaks, one after about two hours (cf. Willstätter and Zechmeister, A., 1913, i, 955), and the other after about six or seven hours. Possibly the three steps in the curves represent successive stages in the degradation of the cellulose; they may also be due to changes in the optical activity of the sugars produced, or perhaps three sugars are formed from the start of the reaction. The relative merits of the three hypotheses cannot be decided from the evidence available. No direct relationship exists between the optical curves and those obtained by estimations of the reducing sugars. The latter show that the reaction slackens, a maximum of dextrose, 85.6—97.8%, being obtained after about twenty-five hours. It is concluded (cf. Cunningham, T., 1918, **113**, 173) that the optical method of determining the quantitative conversion of cellulose into sugar is of little value. It does, however, indicate that considerable differences exist between celluloses from different sources. W. S. N.

**The Viscosity of some Cellulose Acetate Solutions.** ERNEST WALTER JOHN MARDLES (*T.*, 1923, **123**, 1951—1957).

**Lignin.** EMIL HEUSER and ARNE WINSVOLD (*Cellulosechemie*, 1923, **4**, 49—58; 62—68).—On treatment with fused potassium hydroxide, lignin prepared from wood by the method of Willstätter and Zechmeister yielded up to 23% of phenolic derivatives. This suggests a constitution with a benzene nucleus and oxidisable

side-chains. Under similar conditions, cellulose yields only negligible quantities of aromatic derivatives. The most favourable temperature for the fusion is between  $240^{\circ}$  and  $280^{\circ}$ . Various substantial amounts of lignic acids are recovered from the products of the fusion; the phenolic products consist of protocatechuic acid (16–19%) and pyrocatechol (1–3%). If the fusion be conducted in the presence of air, secondary oxidation takes place with formation of oxalic acid (up to 20%). In an indifferent atmosphere, such as hydrogen or nitrogen, the formation of oxalic acid is practically suppressed and the yield of pyrocatechol increases up to 9%. Protocatechuic acid is the primary product of the fusion; the pyrocatechol is formed from it by elimination of carbon dioxide. If the fusion be conducted in an iron vessel, there is a catalytic destruction of the protocatechuic acid, but the formation of pyrocatechol, if air be excluded, is increased up to 23%.

J. F. B.

**Methyl- and Ethyl-ammonium Mercuribromides.** RAYMOND M. HANN (*J. Amer. Chem. Soc.*, 1923, **45**, 1763–1764).—Alkylammonium mercuribromides,  $\text{NR}_4\text{Br.HgBr}_2$ , and alkylammonium dimercuribromides,  $\text{NR}_4\text{Br.2HgBr}_2$ , where  $\text{R}=\text{H}$ , or alkyl, are formed in alcoholic solution from mercuric bromide, an alkyl bromide, and the hydrobromide of an amine. They are far more soluble in organic solvents than the corresponding chlorides and iodides. The presence of chloride-ion, as from an amine hydrochloride, decreases the solubility, but gives products containing both chlorine and bromine.

*Dimethylammonium dimercuribromide*, m. p.  $171-172^{\circ}$ .  
*Diethylammonium dimercuribromide*, heavy, brilliant white plates, m. p.  $158^{\circ}$ .  
*Trimethylammonium mercuribromide*, m. p.  $102^{\circ}$ .  
*Triethylammonium dimercuribromide*, m. p.  $124-125^{\circ}$ .  
*Tetraethylammonium mercuribromide*, m. p.  $72^{\circ}$ .  
 W. S. N.

**Tetramethylammonium Tri- and Tetra-chloroiodides.** WILLIAM NORMAN RAE (*J. Amer. Chem. Soc.*, 1923, **45**, 1725).—Since no polyhalides of the alkali metals or ammonium corresponding with the di-, tri-, and tetra-chloroiodides of tetramethylammonium are known, the author has repeated the work of Weltzien (*Annalen*, 1856, **99**, 1), in which the preparation of these compounds is described. Using the same method as Weltzien, it is shown that the compound described as the trichloroiodide is of variable composition, and that in all probability this substance is a mixture of the di- and tetra-chloroiodides produced by the decomposition of an unstable trichloroiodide. Weltzien's tetra-chloroiodide is judged from the analyses also to have been partly decomposed. The author has obtained a solid which approaches much more closely to the composition demanded by  $\text{NMe}_4\text{ICl}_4$  by the long-continued action of dry chlorine on tetramethylammonium iodide at  $28^{\circ}$ . This compound is an orange-coloured substance which requires about fifty days' treatment as above for its preparation.

J. F. S.

**The Complex Ions formed by Silver Salts and Ammonia or Substituted Ammonias.** P. JOE (*Compt. rend.*, 1923, 176, 1805—1808; cf. this vol., i, 307).—The methods used in the author's previous work have now been applied to the cases of diethylamine and hexamethylenetetramine. The former yields a complex ion of the formula  $\text{Ag}(\text{NHEt}_2)_2^+$  which is slightly less stable than the corresponding ethylenediamine complex. On dilution, the complex ion breaks down and the properties of the resulting solution indicate the formation of  $\text{NHEt}_2\text{Ag}^+$  ions. Hexamethylenetetramine also yields two complex univalent ions,  $\text{Ag}[\text{C}_6\text{H}_{12}\text{N}_4]_2^+$  and  $\text{Ag}[\text{C}_6\text{H}_{12}\text{N}_4]^+$ . Concentrated ammonia yields an ion of the formula  $\text{Ag}(\text{NH}_3)_2^+$ , but the changes undergone by the latter on dilution are less capable of a simple interpretation than with the ions previously mentioned. A brief account is given of the action of change of temperature on the various argento-diamino-ions.  
H. J. E.

**Preparation of Carbamide from Ammonia and Carbon Dioxide.** JEAN LÉON MAURICE FRÉJACQUES (Fr. Pat. 527733; from *Chem. Zentr.*, 1923, ii, 631—632).—Ammonium carbamate is heated under pressure at 145—200°. For example, by the action of ammonia on carbon dioxide with cooling or by the action of liquid ammonia on carbon dioxide, ammonium carbamate is obtained, and heated in an autoclave for two to four hours at 150°. The temperature is allowed to fall to 65—100°, and the ammonia, carbon dioxide, and water from undecomposed ammonium carbamate are removed. Carbamide remains in the autoclave.  
G. W. R.

**The Carbamide Dearrangement.** II. TENNEY L. DAVIS and KENNETH C. BLANCHARD (*J. Amer. Chem. Soc.*, 1923, 45, 1816—1820).—The formation of phenylcarbamide and of *s*-diphenylcarbamide occurs when carbamide and aniline hydrochloride are boiled in aqueous solution. Phenylcarbamide dearranges into diphenylcarbamide when its aqueous solution is boiled, and, if steam is passed through, the distillate contains aniline. This dearrangement of carbamide and its substitution derivatives, which has not previously been observed to occur in solution (but cf. this vol., i, 22), is used in the preparation of various alkyl- and aryl-carbamides.

*s*-Dimethylcarbamide and *s*-diethylcarbamide are formed when carbamide is heated at 160—170° with methylamine hydrochloride or ethylamine hydrochloride, respectively. *s*-Diphenylcarbamide and *s*-phenylethylcarbamide are both produced when diethylcarbamide and aniline are heated at 160—170°; at this temperature, *s*-phenylethylcarbamide passes into *s*-diphenylcarbamide, with evolution of ethylamine. *s*-Di-*n*-butylcarbamide, white flakes, m. p. 70.5—71.0°, is formed when carbamide is boiled in aqueous solution with *n*-butylamine or its hydrochloride. When heated with aniline at 160—170°, it yields *s*-diphenylcarbamide, and a small quantity of a substance, white flakes, m. p. 65°, possibly *s*-phenyl-*n*-butylcarbamide. *s*-Di-*n*-amylcarbamide, white flakes,

m. p. 92·8°, is produced when carbamide and *n*-amylamine hydrochloride are heated at 160—170°; the use of *iso*amylamine hydrochloride gives a *substance*, transparent plates, m. p. 37·5°, evidently *s-diisoamylcarbamide*. Benzylcarbamide is formed when carbamide and benzylamine are heated at 160—170°, or boiled together in aqueous solution, but dibenzylcarbamide is produced only by the first method. Benzylcarbamide does not undergo rearrangement when boiled in aqueous solution. Carbamide does not react in boiling aqueous solution with methylaniline, or when heated with dibutylamine hydrochloride. *as*-Phenylethylcarbamide is produced when carbamide and ethylaniline hydrochloride are boiled in aqueous solution, whilst the use of methylaniline hydrochloride gives *as*-phenylmethylcarbamide.

It is held that these facts support the hypothesis (*loc. cit.*) that unsymmetrically disubstituted carbamides dearrange in only one way,  $RR'N\cdot CO\cdot NH_2 \rightleftharpoons RR'NH + HNCO$ , whilst symmetrically disubstituted carbamides dearrange in two ways,  $R\cdot NH_2 + R'\cdot NCO \rightleftharpoons RNH\cdot CO\cdot NHR' \rightleftharpoons R'\cdot NH_2 + R\cdot NCO$ . W. S. N.

**Preparation of Alkylguanidines.** ROSS PHILLIPS and H. T. CLARKE (*J. Amer. Chem. Soc.*, 1923, 45, 1755—1757).—Methyl isothiocarbamide reacts with methylamine or dimethylamine in warm aqueous solution, with evolution of methyl mercaptan, and formation of, respectively, *methylguanidine sulphate*, m. p. 239—240°, yield 82%, and *αα*-dimethylguanidine sulphate, m. p. 285—288° (decomp.), yield 82%. It is found incidentally that *sodium methyl sulphide*,  $2MeSN_2\cdot 9H_2O$ , long, flat needles, decomp. 200°, crystallises from an aqueous 25% solution of sodium hydroxide when the gas is passed in for purposes of isolation.

W. S. N.

**Alkaline Solutions of Copper Hydroxide [and Silver Oxide].** III. WILHELM TRAUBE (*Ber.*, 1923, 56, [B], 1653—1656).—Complex salts of copper hydroxide with amines and polyhydroxy-compounds have already been shown to exist and to possess a reddish-violet colour characteristic of the presence of copper in both the anion and the cation. It is now shown that similar salts can be obtained containing silver, copper, biuret, and an amine.

*Silver diamminecupribiuret*,  $[Ag(NH_3)_2]_2[Cu(C_2H_3O_2N_3)_2]$ , is prepared by adding freshly prepared silver oxide to a solution of biuret in aqueous ammonia. When the oxide has dissolved, copper hydroxide is added and dissolves to a purple solution which deposits the cupribiuret as red, obliquely truncated prisms.

*Silver ethylenediamminecupribiuret*,  $[Ag(en)]_2[Cu(C_2H_3O_2N_3)_2]$ , is prepared in a similar manner, and forms short, ruby-red prisms, easily soluble in water.

H. H.

**Reactions of Thiocyanates on Ferric Salts and of Ferric Salts on Thiocyanates.** J. CLARENS (*Bull. Soc. chim.*, 1923, [iv], 33, 988—991).—Red ferric thiocyanate is easily soluble in aqueous ether and can be extracted from a dilute aqueous solution

by that solvent. The extract possesses a deep violet colour which may be completely discharged by the addition of ferric chloride. The explanation of this effect put forward by the present author is that an excess of thiocyanate is necessary for the formation of ferric thiocyanate, which is soluble in ether. When a ferric salt is added, this excess of thiocyanate is removed, and a salt of dithiocyanic acid, insoluble in ether, is formed.

H. H.

**An Intercepted Hydrolysis.** OLIVER C. DE C. ELLIS and LESLIE B. GIBBINS (*J. Amer. Chem. Soc.*, 1923, **45**, 1727—1728).—In an attempt to prepare phosphonium cyanide by heating potassium cyanide with phosphorus and a little water, an extremely pure sample of ammonium cyanide was collected in the cooled receiver. The reaction is explained as follows: the equilibrium  $\text{KCN} + \text{H}_2\text{O} \rightleftharpoons \text{KOH} + \text{HCN}$  is destroyed at higher temperatures by the disappearance of the hydrogen cyanide; this is due to a further hydrolysis,  $\text{HCN} + 2\text{H}_2\text{O} = \text{HCO}_2\text{NH}_4$ , and  $\text{HCO}_2\text{NH}_4 = \text{NH}_3 + \text{HCO}_2\text{K} + \text{H}_2\text{O}$ . The total reaction of boiling potassium cyanide in water is  $\text{KCN} + 2\text{H}_2\text{O} = \text{NH}_3 + \text{HCO}_2\text{K}$ . When phosphorus is present, the hydrolysis is interrupted to an extent defined by the reaction of the phosphorus with the potassium hydroxide present, an equivalent amount of hydrogen cyanide being liberated. Thus the two main reactions of the preparation are  $\text{KCN} + 2\text{H}_2\text{O} = \text{NH}_3 + \text{HCO}_2\text{K}$  and  $3\text{KCN} + 4\text{P} + 6\text{H}_2\text{O} = 3\text{KH}_2\text{PO}_3 + \text{PH}_3 + 3\text{HCN}$ . If the phosphorus is replaced by aluminium, the yield of ammonium cyanide is greater, particularly if a suitable quantity of sulphuric acid be added. In some cases, the product was coloured, due to presence of azulmic acid, thus showing the great readiness with which ammonia is oxidised.  $2\text{NH}_4\text{CN} + \text{O} = 2\text{NH}_3 + \text{C}_2\text{N}_2 + \text{H}_2\text{O}$ ;  $\text{NH}_4\text{CN} \rightleftharpoons \text{NH}_3 + \text{HCN}$ ;  $2\text{NH}_3 + 2\text{C}_2\text{N}_2 = \text{C}_4\text{H}_6\text{N}_6$ ;  $\text{C}_4\text{H}_6\text{N}_6 + \text{H}_2\text{O} = \text{C}_4\text{H}_5\text{N}_5\text{O} + \text{NH}_3$ . Ammonium cyanide is readily ignited, burning with a pale fawn-coloured flame. It immediately decolorises neutral potassium permanganate solution; it reacts with a chloroform solution of sulphur, yielding ammonium thiocyanate.

J. F. S.

**Oxidation Phenomena among the Complex Cyanides of Nickel; Valency, Co-ordination, Colour.** ANDRÉ JOB and ANDRÉ SAMUEL (*Compt. rend.*, 1923, **177**, 188—191).—The red solution obtained on reducing a nickelocyanide by means of an alkali metal amalgam contains the compound  $\text{K}_2[\text{Ni}(\text{CN})_3]$ , where nickel is univalent and has a co-ordination number of 3. The formation, simultaneously, of potassium cyanide is proved by the fact that nickelous cyanide dissolves in the solution to give dipotassium nickelocyanide,  $\text{K}_2[\text{Ni}(\text{CN})_4]$ . The red solution, moreover, absorbs carbon monoxide (and also acetylene), forming an almost colourless solution containing univalent nickel with co-ordination number 4, i.e., containing the complex group  $[\text{Ni}(\text{CN})_3\text{CO}]$ , no potassium cyanide being liberated in this case. Similarly, cobaltous cyanide, potassium cyanide, and carbon monoxide combine to form the *carbonylcobaltocyanide*.

The instability ascribed in the literature to the above red solution

is due to the presence of free cyanide-ions, and is more marked if an excess of potassium cyanide is added. Again, on shaking the red solution with air it becomes pale yellow and nickelous cyanide is precipitated:  $2K_2[Ni(CN)_3] + O + H_2O = Ni(CN)_2 + K_2[Ni(CN)_4] + 2KOH$ , so that the dissolved nickel remaining is bivalent, with co-ordination number 2.

The yellow nickelocyanide solution becomes bright red when treated with an excess of potassium cyanide, owing to the formation of *tetrapotassium nickelocyanide*,  $K_4[Ni(CN)_6]$ , containing bivalent nickel with co-ordination number 6. The doubt hitherto cast on the existence of this salt is due to the fact that evaporation leads to the separation of potassium cyanide and nickelocyanide. Similarly, in dilute solutions, the complex dissociates, so that conductivity measurements are then equally untrustworthy.

When nitric oxide is passed into a solution of potassium nickelocyanide, the colour first fades and then becomes an intense violet. This is due to reduction of nitric oxide to hydroxylamine. Thus, the violet solution is obtained by dissolving potassium nickelocyanide (1 mol.) in water, adding a suspension of nickelous cyanide (1 mol.), and then 3 molecules of hydroxylamine and 6 molecules of potassium hydroxide. To the violet compound (nickel tervalent, co-ordination number 6) is given the provisional formula  $K_2[Ni(CN)_3(OH)_2(NH_2 \cdot OH)]$ .  
E. E. T.

**Dissociation of Complex Cyanides.** GEORGE JOSEPH BURROWS (T., 1923, 123, 2026—2029).

**Reaction of Hydroxylamine with Nitroprussides.** J. GIRAL PEREIRA (*Anal. Fis. Quim.*, 1923, 21, 236—244).—When hydroxylamine hydrochloride is allowed to react with a solution of sodium nitroprusside in the presence of sodium hydroxide, free from carbonate, under conditions described, a red coloration is given accompanied by evolution of nitrogen with effervescence. On addition of ethyl alcohol, a red, glutinous mass separates. A description is given of its reactions with various substances. Its formation is discussed and the formula  $Fe \begin{smallmatrix} C(NNa) \cdot C(NNa) \\ C(NNa) \cdot C(NNa) \end{smallmatrix} C:N:NO$  is suggested.  
G. W. R.

**The Catalytic Reduction of Semicarbazones.** K. A. TAIPAL and S. A. SMIRNOFF (*Ber.*, 1923, 56, [B], 1794—1798).—1-Alkyl-semicarbazides are prepared by the catalytic hydrogenation of the semicarbazones of aliphatic aldehydes in the presence of platinum black and alcohol or, preferably, glacial acetic acid. The  $\beta$ -isomerides have, in general, lower melting points than the corresponding  $\alpha$ -compounds. Like the latter, they reduce ammoniacal silver solution at the atmospheric temperature; Fehling's solution is reduced slowly when cold, rapidly when heated.

$\alpha$ -Ethylsemicarbazide,  $NH_2 \cdot CO \cdot NH \cdot NHEt$ , crystallises in small, transparent prisms, m. p. 97—98°; the corresponding *hydrochloride*, a microcrystalline powder, m. p. 148—150°; the *hydrogen oxalate*,  $C_5H_{11}O_5N_3$ , matted needles, decomp. 165.5°; the *benzoyl*

derivative,  $C_{10}H_{13}O_2N_3$ , m. p. 205—206°, and the *acetyl* compound, m. p. 218.5°, are described; a nitroso-derivative could not be obtained. The action of saturated barium hydroxide solution on the *acetyl* derivative leads to the formation of 3-hydroxy-5-methyl-1-ethyl-

1:2:4-triazole,  $\begin{matrix} N=CMe \\ | \\ C(OH).N \end{matrix} > NEt$  or  $\begin{matrix} N=CMe \\ | \\ CO-NH \end{matrix} > NEt$ , aggregates of

needles, m. p. 123°; the corresponding amorphous *silver* salt and the *hydrochloride*, m. p. about 220—221° (decomp.) when rapidly heated, are described. 1-n-Propylsemicarbazide has m. p. 79.5—80° (*hydrochloride*, m. p. 160.5—161°). H. W.

**The Application of Colloidal Platinum as Catalyst in the Reduction of Azines, Semicarbazones, and Phenylhydrazones.** H. L. LOCHTE and J. R. BAILEY (*Ber.*, 1923, 56, [B], 1799—1800; cf. A., 1922, i, 329; this vol., i, 26).—A claim for priority against Taipale (this vol., i, 547).

The reduction of dimethylketazine to  $\beta$ -hydrazopropane has been effected by Taipale in glacial acetic acid solution. The reaction is more conveniently effected in the presence of hydrochloric acid when a mixture of acetone and hydrazine hydrate can be used, thus avoiding the preliminary isolation of dimethylketazine. The oxidation of  $\beta$ -hydrazopropane by hydrogen peroxide yields the azo-compound,  $CHMe_2.N:N.CHMe_2$ , and not acetoneisopropylhydrazone as indicated by Taipale. The latter substance has been prepared as a colourless, mobile liquid with a pronounced odour of menthol, b. p. 132—134°/750 mm. H. W.

**Manufacture of Hydroxylated Aliphatic Arsinic Acids.** LES ÉTABLISSEMENTS POULENC FRÈRES and CARL OECHSLIN (*Brit. Pat.* 191028).—Compounds such as  $HO.CH_2.CH_2.AsO_3H_2$ ,  $C_2H_5(OH).AsO_3H_2$ ,  $OH.C_3H_7(AsO_3H_2)_2$ , are obtained by the action of an alkali arsenite on an aliphatic hydrocarbon containing one or more halogen atoms and one or more hydroxyl groups (e.g. glycol chlorohydrin, glycerol mono- and di-chlorohydrin, epichlorohydrin) and decomposing the alkali salt by acidification. W. T. K. B.

**A New Organo-metallic Compound: Diplumbic Hexaethyl.** THOMAS MIDGLEY, jun., CARROLL A. HOCHWALT, and GEORGE CALINGAERT (*J. Amer. Chem. Soc.*, 1923, 45, 1821—1823).—Lead triethyl hydroxide is prepared by the action of sodium hydroxide solution on lead triethyl chloride; a 30% solution in 95% ethyl alcohol is electrolysed, using lead electrodes and a current density of 0.01 amp./sq. cm. *Diplumbic hexaethyl*, a heavy, yellow oil, b. p. about 100°/2 mm., is formed at the cathode, much gas being evolved at the anode,  $2PbEt_3.OH = Pb_2Et_6 + H_2O + O$ . The oil is easily decomposed by air, giving a yellow powder which rapidly darkens;  $d$  1.94. The oil is bimolecular in concentrated benzene solution, but unimolecular in very dilute solution. It reacts with hydrochloric acid, giving lead triethyl chloride, lead chloride, and a gas, probably according to the equation  $Pb_2Et_6 + 3HCl = PbEt_2Cl + PbCl_2 + 3C_2H_6$ . W. S. N.

**The Low-temperature Tar obtained from the Zeche Fürst Hardenberg Coal and, in Particular, the Content of Benzene, Phenol, and Acetone.** HANS BROOKE (*Ber.*, 1922, 56, [B], 1787—1791).—According to Schütz (this vol., i, 195, 452), the low-temperature tar derived from Zeche Fürst Hardenberg coal contains a much greater proportion of benzene, carbolic acid, and acetone than has been observed previously in low-temperature tars by Fischer and his co-workers. The author has therefore re-examined the tar produced from this coal in experimental, rotary furnaces, and finds that it does not contain more than 0.04% of benzene (calculated on the tar) and 0.16% of carbolic acid. It does not yield more than 50 g. of acetone per ton of coal. The low-temperature tar from the Hardenberg coal therefore closely resembles other low-temperature tars.

H. W.

**Naphthenes in their Behaviour towards Catalytic Dehydrogenation. The Nature of Petroleum.** N. ZELINSKI (*Ber.*, 1923, 56, [B], 1718—1723).—Octanaphthene is practically unchanged by platinum black at 300—310°; treatment of the specimen with fuming sulphuric acid containing 10% of sulphur trioxide shows that it contains at least 15—20% of octanes. *iso*-Octanaphthene is similarly unchanged in the presence of platinum black at 300°; the natural hydrocarbon appears to be closely related to that obtained from heptanaphthenecarboxylic acid. The similarity in the behaviour of octanaphthene and *iso*-octanaphthene towards catalytic dehydrogenation justifies the conclusion that their ring systems are identical or very closely related. Nonanaphthene undergoes only slight dehydrogenation in the presence of palladium black at 300—310°; after removal of other cyclic compounds by fuming sulphuric acid, the residual hydrocarbon is a mixture containing not less than 50% of open-chain compounds.

1:4-Dimethyl-2-ethylcyclopentane is partly dissolved by fuming sulphuric acid (10%  $\text{SO}_3$ ) to yield a dark-coloured solution; the change occurs without marked development of heat and without evolution of sulphur dioxide. *cyclopentane* is passive under similar conditions, whereas the hexahydroaromatic hydrocarbons become oxidised. The behaviour towards fuming sulphuric acid appears to be a trustworthy criterion for discriminating between *cyclopentanes* and *cyclohexanes*. The author is drawn to the conclusion that naphthenes prepared from naphthenic acids and the natural naphthenes of petroleum consist mainly of cyclic compounds and not of hexahydroaromatic hydrocarbons.

H. W.

**The Behaviour of 1:1-Dimethylcyclohexane towards Catalytic Dehydrogenation.** N. ZELINSKI [with (FRL.) N. DELZOVA] (*Ber.*, 1923, 56, [B], 1716—1718).—1:1-Dimethylcyclohexane, b. p. 118.5—120°,  $d_4^{20}$  0.7820,  $n_D^{20}$  1.4342, is not affected by passage over extremely active, platinised asbestos at 300°. Since the hydrocarbon does not belong to the hexahydroaromatic series (owing to the presence of the two methyl groups attached to the same carbon atom), this observation is in harmony with the authors'

theory of the pronouncedly selective nature of catalytic dehydrogenation and of its exclusive applicability to hexahydroaromatic compounds.

H. W.

**Parallelism between the Mobility of the Hydrogen of the Benzene Nucleus and that of Chlorine of the Side Chain.**

S. C. J. OLIVIER (*Rec. trav. chim.*, 1923, 42, 775—778).—A résumé and discussion of previously published work on the ease with which the halogens are removed from the benzene nucleus and from side chains in the presence of other substituting groups (A., 1922, i, 646; this vol., i, 179, 769).

J. F. S.

**The Sulpho-chromic Oxidation of Aromatic Hydrocarbons and the Structural Conception of Graphite.**

L. J. SIMON (*Compt. rend.*, 1923, 177, 265—268; cf. this vol., i, 81; also Simon and Guillaumin, this vol., ii, 432).—Sulpho-chromic oxidation of a series of hydrocarbons shows that with the use of silver dichromate good values are obtained with those of aromatic structure. Chromic anhydride yields an "oxidation deficit" in each case; this varies within comparatively small limits except in the cases of naphthalene and phenanthrene and differs for isomerides, e.g., diphenyl and acenaphthene. Other hydrocarbons are clearly distinguished from those in the aromatic series by giving results which are very considerably below the theoretical value. A table of the figures obtained with different varieties of carbon is given (cf. this vol., ii, 506), from which the conclusion is drawn that as the "oxidation deficit" of graphite is about one-third, it is possible to oxidise it in three stages. This, added to the fact that the results with graphite are of the same order as those given by aromatic hydrocarbons, is regarded as furnishing additional evidence in support of the hexagonal structure of graphite and possibly indicating that two carbon atoms in the ring are somewhat different in their properties from the remaining four.

H. J. E.

**Influence of Substitution in the Components on Equilibrium in Binary Solutions. XLI. Equilibrium in Binary Solutions of the Isomeric Dinitrotoluenes with Amines and Hydrocarbons.**

ROBERT KREMANN, EUGEN HÖNIGSBERG, and OTTO MAUERMANN (*Monatsh.*, 1923, 44, 65—81).—The tendency of dinitrotoluenes to form additive compounds with amines and with hydrocarbons is, as would be expected, intermediate between that of the mono- and tri-nitrotoluenes. Of the four dinitrotoluenes (2:4-, 2:6-, 3:5-, and 3:4-), the 3:5-derivative most readily, and the 2:6-derivative least readily forms additive compounds, thus illustrating Kremann's theory of steric valency hindrance.

3:4-Dinitrotoluene forms simple eutectics with the following compounds (a percentage given, throughout this abstract, is that of the second, variable, component in the different series): aniline, (—17°, 69%), *p*-toluidine (11°, 41%),  $\beta$ -naphthylamine (33°, 28%),  $\alpha$ -naphthylamine (—10°, 54%), acenaphthene (39°, 30%), anthracene (55°, 2%), and fluorene (37°, 29%).

2:6-Dinitrotoluene forms simple eutectics with *p*-toluidine

(18°, 55%),  $\alpha$ -naphthylamine (7.5°, 62%),  $\beta$ -naphthylamine (45°, 24%), anthracene (54°, 6%), fluorene (46°, 30%), and acenaphthene (46°, 27%).

3:5-Dinitrotoluene is best prepared by slowly adding aceto-*p*-toluidide to eight times its weight of nitric acid (*d* 1.79), at a temperature not exceeding 0°, purifying the dinitro-derivative by hot benzene extraction, hydrolysing it with concentrated sulphuric acid (not above 90°), diazotising the resulting base at -10° in concentrated sulphuric acid-absolute alcohol solution, warming, and purifying the dinitrotoluene by extraction with alcohol.

The additive power of 3:5-dinitrotoluene is shown by the following: Aniline, equimolecular compound, m. p. 46.5°, eutectics with the two components at 46°, 32% and at -13°, 92% (cf. A., 1906, ii, 268); compound formation is not well indicated by the results obtained. *p*-Toluidine, equimolecular compound, m. p. 25°, eutectic with *p*-toluidine at 22°, 61%; the indications of compound formation are indefinite in this case also.  $\alpha$ -Naphthylamine, equimolecular compound, m. p. 107-108°, eutectic with the two components at 75°, 12%, and at 40°, 87%.  $\beta$ -Naphthylamine, equimolecular compound, m. p. about 53°, undergoing extensive dissociation in the fused state: eutectics at 53°, 27%, and at 53°, 40%. Acenaphthene, equimolecular compound, m. p. 94°, eutectics with the two components at 72°, 15%, and at 79°, 73%. Fluorene and anthracene give simple eutectics only, at 42°, 39%, and at 76°, 14%, respectively.

2:4-Dinitrotoluene and *p*-toluidine form only a simple eutectic at 15°, 50%.

E. E. T.

**Freezing-point Diagram of Mixtures of Trinitrotoluene and Picric Acid.** C. A. TAYLOR and W. H. RINKENBACH (*Ind. Eng. Chem.*, 1923, 15, 795).—The freezing-point curve of mixtures of pure trinitrotoluene and pure picric acid is given. There is a eutectic point at 69.8% of trinitrotoluene (59.4°). No molecular compounds are formed.

H. C. R.

***p*-Chlorodiphenylsulphone.** HAEHL (*Compt. rend.*, 1923, 177, 194-195).—The author shows that the product obtained by Beckurts and Otto (cf. A., 1886, 1031, etc.) by the action of benzene-sulphonyl chloride on chlorobenzene in presence of aluminium chloride is *p*-chlorodiphenylsulphone. Sulphanilic acid is converted into *p*-chlorobenzenesulphonic acid, the chloride of this acid being condensed, in presence of aluminium chloride, with benzene. The product is identical with that described by the older workers.

E. E. T.

**Hydrogenation of the Diphenyl Nucleus.** J. RANEDO and A. LEON (*Anal. Fís. Quím.*, 1923, 21, 270-279).—The catalytic hydrogenation by the Willstätter method of diphenyl and *p*-diphenyl-carboxylic acid was studied, using platinum black as catalyst. With partial hydrogenation, mixtures were produced in each case. Complete hydrogenation of diphenyl gives a liquid, b. p. 226-228°, presumably dodecahydrodiphenyl. *p*-Diphenylcarboxylic acid, by complete hydrogenation, yields a mixture of two isomeric acids, one

having m. p. 105° (needles) and the other m. p. 76–78° (scales). The amide of the acid of m. p. 105° was prepared; it forms crystals, m. p. 197°. G. W. R.

**Bromodiphenylmethane and the Grignard Reaction.** L. BERT (*Compt. rend.*, 1923, 177, 324–326; cf. Gomberg and Cone, A., 1906, i, 414).—Magnesium, if previously activated by means of ethyl bromide, readily reacts with bromodiphenylmethane in ethereal solution to give a precipitate of *s*-tetraphenylethane [yield, 70%; m. p. 212.5° (cf. Biltz, A., 1893, i, 718)]. Mere traces of magnesium diphenylmethyl bromide are formed, and in order to utilise the bromo-compound for Grignard reactions, the second component must be present from the outset. Thus, when carbon dioxide is allowed to pass through a reacting mixture of the bromo-compound, magnesium, and ether, and the product is decomposed in the usual manner, a mixture of diphenylacetic acid and tetraphenylethane results. E. E. T.

**Chromoisomerism in the Stilbene Series.** NICHOLAS MICHAEL CULLINANE (T., 1923, 123, 2053–2060).

**Decahydronaphthalene and its Behaviour towards Catalytic Dehydrogenation.** N. ZELINSKI (*Ber.*, 1923, 56, [B], 1723–1724).—Decahydronaphthalene is smoothly prepared by passing tetrahydronaphthalene and hydrogen over platinised asbestos at 150–160° or palladium black at 120°. It is very readily dehydrogenated by palladium black at the atmospheric pressure and 300°, whereby naphthalene is produced. The formation of intermediate substances of unsaturated character could not be observed. H. W.

**The Structure of the Benzene Nucleus. IV. The Reactivity of Bridged Linkings.** CHRISTOPHER KELK INGOLD (T., 1923, 123, 2081–2088).

**The Structure of the Benzene Nucleus. III. Synthesis of a Naphthalene Derivative involving a Bridged Phase of the Nucleus. The Constitution of Naphthalene and Anthracene.** WILLIAM ARTHUR PERCIVAL CHALLENGER and CHRISTOPHER KELK INGOLD (T., 1923, 123, 2066–2081).

**Catalytic Oxidation of Naphthalene at High Temperatures.** TOKISHIGE KUSAMA (*J. Chem. Soc. Japan*, 1923, 44, 605–651).—In preparing phthalic anhydride from naphthalene by catalytic oxidation, the author has studied the effect on the catalyst of the temperature of reaction, the ratio of the oxidisable compound and the oxygen, the time of contact of the mixed gas and vapour and the catalyst, and the addition of an inert gas to the mixture. As catalysts, oxides of vanadium and molybdenum were found to be most suitable, and they act better when mixed with other oxides than when used singly. The best results were obtained by the use of vanadium oxide containing a small amount of molybdenum oxide. During the course of reaction, the temperature of the catalyst varies locally, the front part of the catalyst having usually a higher

temperature than the rear. The course of the reaction is indicated by a temperature curve drawn by taking the temperatures as ordinates and the distance of the catalyst from one end as abscissæ; If there is a sharp maximum in the front portion of the curve, complete combustion predominates, but if the curve shows a gradual elevation with a maximum at the rear, it indicates that the reaction is proceeding smoothly, and that a good yield is being obtained. From the form of the temperature curves, the relative value of the different catalysts can be compared and the course of the reactions is indicated. When a mixture of vanadium and molybdenum oxides is used as the catalyst and air as the source of oxygen, complete combustion is minimal at 280–400°. When the catalyst is used in a continuous layer, good yields are obtained by lowering the temperature of the front part of the catalyst and increasing the velocity of a mixture of naphthalene vapour and air. By a discontinuous arrangement of the catalyst, complete combustion is prevented and a good yield is obtained.

K. K.

**Rules of Substitution in the Naphthalene Nucleus.** V. VESELÝ and M. JAKEŠ (*Bull. Soc. chim.*, 1923, [iv], 33, 955–962).—An attempt to apply to the naphthalene molecule a modified form of the Crum Brown and Gibson rule for substitution in the benzene nucleus. Two types of directive substituent are distinguished :

(a) The quinonoid type corresponding with the ortho-para type in the benzene series and including the same radicals. In this class, a quinonoid derivative is always formed if possible. That is to say, if the original substituent is in the 1 position, the second group will enter the 2, 4, 5, or 7 position. If the original group is in the 2 position, the entering group will occupy the 1, 3, 6, or 8 position. As the 1:4- and 1:2-derivatives are the most stable quinonoid forms, so it is found that these preponderate, if possible, in the mixture of isomerides formed.

(b) The non-quinonoid type, corresponding with the meta directing substituents in the benzene series and including the same groups. In this class, there is a predisposition to form 1:3-, 1:6-, 1:8-, and 2:7-derivatives.

The above rules do not apply to tri-substitution, and are not rigid even for di-substitution. Examples are given to show how far they are followed, and conversely.

H. H.

**Some Substitution Reactions of 2-Nitronaphthalene.** V. VESELÝ and M. JAKEŠ (*Bull. Soc. chim.*, 1923, [iv], 33, 952–955).—Direct bromination of 2-nitronaphthalene leads to the formation of 5-bromo-2-nitronaphthalene, the identity of which with the compound obtained by the Sandmeyer reaction on the diazonium sulphate of 2-nitro-5-naphthylamine is established. Nitration of 2-nitronaphthalene in sulphuric acid solution is unsuitable for the preparation of dinitro-derivatives because considerable quantities of 1:3:8-trinitronaphthalene are formed, and, in addition, some of the original nitro-compound undergoes sulphonation. A mixture of 2:6- and 2:8-dinitronaphthalenes is obtained by nitration of 2-nitronaphthalene in boiling glacial acetic acid. The mixture

of isomerides so obtained may be separated by crystallisation from concentrated sulphuric acid.

H. H.

**Studies in the Anthracene Series.** V. EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and MARCUS AURELIUS MATTHEWS (T., 1923, 123, 1994—2008).

**The Action of Grignard's Compounds on Anthrone.** F. KROLLPFEIFFER and F. BRANSCHIED (*Ber.*, 1923, 56, [B], 1617—1619).—The action of an excess of Grignard's reagents in cold ethereal solution on anthrone leads to the formation of substituted 9-hydroxy-9 : 10-dihydroanthracenes,  $C_6H_4 \begin{smallmatrix} < CR(OH) > \\ < CH_2 > \end{smallmatrix} C_6H_4$ , which are converted when the mixtures are heated to gentle boiling into substituted *ms*-anthracenes,  $C_6H_4 \begin{smallmatrix} < CR > \\ < CH > \end{smallmatrix} C_6H_4$ .

The following individual substances are described: 9-Methylanthracene, pale, greenish-yellow needles, m. p. 79—80°. 9-Hydroxy-9-ethyl-9 : 10-dihydroanthracene, coarse, colourless crystals, m. p. 87°. 9-Ethylanthracene, colourless leaflets with blue fluorescence, m. p. 59°. 10-Chloro-9-ethylanthracene (prepared by chlorination of a solution of 9-ethylanthracene in ice-cold chloroform), pale greenish-yellow needles, m. p. 111°. 9-Hydroxy-9-isoamyl-9 : 10-dihydroanthracene, coarse, colourless crystals, m. p. 94—95°. 9-Isoamylanthracene, pale green needles with blue fluorescence, m. p. 61°. 9-Hydroxy-9-phenyl-9 : 10-dihydroanthracene, coarse, colourless crystals, m. p. 112—113°. 9-Phenylanthracene, lustrous, pale yellow leaflets, m. p. 151—152°. H. W.

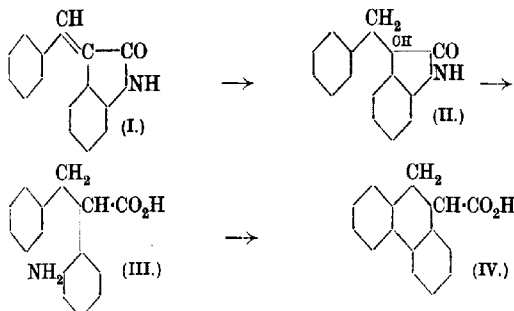
**The Action of Grignard's Compounds on Anthrone.** A. SIEGLITZ and R. MARX (*Ber.*, 1923, 56, [B], 1619—1621).—The action of magnesium alkyl halides on anthrone has been examined under conditions which differ somewhat from those adopted by Krollpfeiffer and Branschied (preceding abstract). A lukewarm solution of anthrone in anhydrous, thiophen-free benzene is added gradually to a cold solution of three molecular proportions of the Grignard reagent in ether. The product is decomposed with ice-cold water and dilute sulphuric acid. The benzene-ether layer is washed with sodium hydroxide solution and the solvent is allowed to evaporate slowly; by-products such as anthraquinone and dianthrone separate first, followed by the alkylanthracene derivatives.

The following individual substances are described: 9-Methylanthracene, pale yellow prisms or needles, m. p. 81.5°, b. p. 196—197°/12 mm. [*picrate*, dark, brownish-red needles, m. p. 137° (decomp.)]. 9-Methyl-9 : 10-dihydroanthracene, prepared by reduction of 9-methylanthracene by sodium and alcohol, long, colourless needles, m. p. 61.5—62°. 9-Hydroxy-9-ethyl-9 : 10-dihydroanthracene, large, transparent rhombohedra, m. p. 88—89°. 9-Ethylanthracene, colourless leaflets, m. p. 59°, b. p. 189—191°/11 mm. 9-n-Propylanthracene, colourless needles, m. p. 69—70° [*picrate*, brownish-red needles, m. p. 113.5—114.5° (decomp.)].

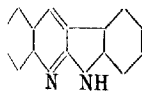
9-*n*-Propyl-9:10-dihydroanthracene, a colourless liquid, b. p. 175—176°/11 mm. 9-*n*-Butylanthracene, long, colourless needles, m. p. 49—50° (picrate,  $2C_{18}H_{18}, C_8H_7O_2N_3$ , dark, brownish-red needles, m. p. 82°). 9-*n*-Butyl-9:10-dihydroanthracene, a colourless liquid with blue fluorescence, b. p. 191—192°/11 mm. H. W.

#### A New Synthesis of Dihydrophenanthrene Derivatives.

E. KIRCHNER (*Nachr. K. Ges. Wiss. Göttingen*, 1921, 154—161; from *Chem. Zentr.*, 1923, i, 944—945).—In order to study the constitution of colchicine, the author has devised a new synthesis of dihydrophenanthrenecarboxylic acid. Benzylideneoxindole (I) from benzaldehyde and oxindole, is hydrogenated to benzylloxindole, (II), which forms white needles, m. p. 130°. By heating with barium hydroxide  $\alpha$ -benzyl-*o*-aminophenylacetic acid (III) is obtained. This is diazotised and the product heated at 50°. By the action of ammonia, a product is obtained from which, on distillation under reduced pressure at 170—270°, dihydrophenanthrenecarboxylic acid (IV) is obtained. It has m. p. 127—130° and gives phenanthrene by distillation with calcium oxide.



The acid portion also contains benzylisocoumaranone,  $C_{13}H_{12}O_2$ , m. p. 58—59°. The neutral portion contains a compound,  $C_{15}H_{16}O_2$  (?), which forms yellow crystals, m. p. 225°. In the place of benzaldehyde as a starting point, its hydroxy- and methoxy-derivatives may be used. In similar manner, starting from  $\alpha$ -phenyl- $\beta$ -*o*-aminophenylpropionic acid, the lactone of  $\alpha$ -phenyl- $\beta$ -*o*-hydroxyphenylpropionic acid, and from that 3-phenyldihydrocoumarin, m. p. 122—123°, may be obtained. From nitrobenzaldehyde, by condensation, *o*-aminobenzylloxindole is obtained at first and then periquindoline (annexed formula).



The latter has m. p. above 290°. The acetyl derivative forms white needles, m. p. 185°. *o*-Nitrobenzylideneoxindole forms reddish-yellow needles, m. p. 225°. Its hydrochloride has m. p. 280°. G. W. R.

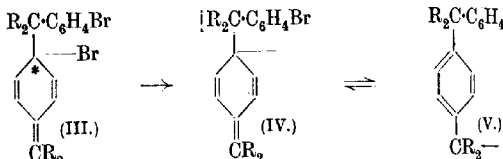
**Triphenylmethyl. XXXIII. Quinoidation of the Triaryl-methyls.** M. GOMBERG and F. F. BLICKE (*J. Amer. Chem. Soc.*, 1923, 45, 1765—1779).—*p*-Bromodiphenyl- $\alpha$ -naphthylcarbinol, di-

phenyl-4-bromo- $\alpha$ -naphthylcarbinol, and the corresponding chlorides have been synthesised, and these compounds, and *p*-bromotriphenylmethyl chloride, have been closely investigated. Incidentally, *p*-bromophenylchrysofluorene has been prepared and its constitution proved.

Prolonged reaction between *p*-bromotriarylmethyl chlorides, in solution, and excess of molecular silver, results first in the removal of one atom of carbinol chlorine with formation of a bluish-violet coloration; half an atomic proportion, but no more, of nuclear bromine is subsequently eliminated, giving an intensely blue solution (cf. Gomberg and Cone, A., 1906, i, 822). The mobility of the nuclear bromine atom, the fact that only half the bromine is removed, and the colour changes are explained on the following hypothesis. The colourless, free, benzenoid radicle, I, formed by the loss of the carbinol chlorine atom, exists in tautomeric equilibrium with its coloured, quinonoid modification, II;



by the union of I with II, a bimolecular form, III, is produced, in which the carbon atom marked \* has aliphatic properties:



Consequently, the bromine attached thereto is removable by means of silver, with production of the free, quinonoid, "second-order" radicle, IV; this, like its "first-order" analogue, II, is in tautomeric equilibrium with the individual, V, which represents the final product, in solution, of the action of silver on a *p*-bromotriarylmethyl chloride.

The correctness of this hypothesis is confirmed by experiments on the absorption of oxygen, the results of which are exhibited graphically. After the removal of the first (carbinol) halogen atom, the amount of oxygen absorbed by the solution corresponds with that calculated for the free radicle,  $R_2C-$ , but the substance which results from the further elimination of half the nuclear bromine absorbs, in solution, only half that amount, i.e., the quantity demanded by the more complex radicle,  $R_2C-C_6H_4-CR_2-$ . Actually the peroxides corresponding with the two types of radicle have been isolated and described.

Baeyer's criticism (A., 1907, i, 691) of the quinonoid hypothesis to account for the removal of nuclear halogen from coloured salts of *p*-halogentriarylmethylcarbinols (Gomberg, A., 1907, i, 504) has been met by showing that prolonged action between silver sulphate and the three colourless carbinyl chlorides investigated causes elimination of both the carbinol and the whole of the nuclear



*methyl chloride*, m. p. 160—161°, gives a deep green coloration with sulphuric acid. Attempts to isolate free radicles have not been successful, but the following peroxides are described. Those of the simple radicles are obtained by the atmospheric oxidation of the solution in which the carbonyl chloride has been agitated with finely divided silver for twenty minutes; if the reaction is allowed to continue for forty-eight to sixty hours, peroxides of the complex radicles are obtained. *p-Bromodiphenyl- $\alpha$ -naphthylmethyl peroxide* has m. p. 146° (decomp.). The flocculent peroxide of the second-order radicle,  $[\text{CPh}(\text{C}_6\text{H}_4\text{Br})(\text{C}_{10}\text{H}_7)\cdot\text{C}_6\text{H}_4\cdot\text{CPh}(\text{C}_{10}\text{H}_7)]_2\text{O}_2$ , decomposes indefinitely at about 120°. *Diphenyl-1-bromo- $\alpha$ -naphthylmethyl peroxide* has m. p. 153—154° (decomp.). The amorphous peroxide,  $(\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CPh}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CPh}_2)_2\text{O}_2$ , decomposes at 135°, and melts indefinitely. W. S. N.

**Attempted Syntheses of Meta-related Ring Systems.**  
F. REINDEL and F. SEGEL (*Ber.*, 1923, 56, [B], 1550—1557).—Attempts to prepare *m*-dibenzylbenzene and to cause *m*-xylylene bromide to react with amines, phenols, and thiophenols are described. The experiments have not up to the present led to the isolation of compounds containing rings closed in the meta-position of the benzene nucleus.

The action of aluminium chloride on *m*-xylylene bromide in the presence of benzene yields mainly diphenylmethane accompanied by smaller amounts of *p*-dibenzylbenzene, anthracene, and mixtures of very viscous, fluorescent liquids. It is very improbable that the latter contain *m*-dibenzylbenzene or that the product isolated by Smythe (T., 1922, 121, 1270), which has been tentatively considered to be *m*-dibenzylbenzene, consists actually of this substance. *iso*Phthalyl chloride, m. p. 42—43°, b. p. 143—144°/13 mm., is conveniently prepared from *isophthalic acid* and thionyl chloride, and is converted by the Friedel-Crafts reaction into *isophthalophenone*. The latter substance is unexpectedly resistant towards reduction with amalgamated zinc and hydrochloric acid; under similar conditions terephthalophenone is transformed only to a very small extent into *p*-dibenzylbenzene.

*m*-Xylylene bromide reacts with *o*-nitroaniline in the presence of boiling chloroform to give an almost quantitative yield of *di-o'-nitrophenyl-m-xylylenediamine*,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{NO}_2)_2$ , yellow needles, m. p. 146—148°. *Di-m'-nitrophenyl-m-xylylenediamine*, yellow leaflets, m. p. 142—145°, is prepared in a similar manner, but in very poor yield.

*m*-Xylylene bromide is transformed by phenol in alcoholic solution in the presence of sodium ethoxide into *m-xylylenyl diphenyl ether*,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{OPh})_2$ , colourless leaflets, m. p. 71—76°. Under similar conditions, *m*-nitrophenol yields *m-xylylenyl di-m'-nitrophenyl ether*, almost colourless needles, m. p. 100—102°. Attempts to isolate the corresponding *m'*-amino-compound were unsuccessful; its *acetyl* derivative, colourless leaflets, m. p. 165—170°, is prepared by acetylation of the crude base or by the action of *m*-xylylene bromide on *m*-acetylaminophenol.

*m*-Xylylenedithioglycol diphenyl ether,  $C_6H_4(CH_2SPh)_2$ , colourless effluets, m. p. 78–82°, is quantitatively prepared from *m*-xylylene bromide and thiophenol. The compound, as also *m*-xylylenyl diphenyl ether, is very resistant towards oxidising agents, but is converted by sodium dichromate and dilute sulphuric acid at 170–180° into the corresponding disulphone,  $C_6H_4(CH_2SO_2Ph)_2$ , long, colourless rods, m. p. 163–165°, phenylbenzylsulphone-*m*-carboxylic acid,  $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot SO_2Ph$ , m. p. 188–192°, and isophthalic acid. H. W.

**Action of Ammonia and Amines on 3 : 4-Dinitrodimethylaniline and 3 : 4-Dinitrodiethylaniline.** P. VAN ROMBURGH (*Rec. trav. chim.*, 1923, 42, 804–807).—Alcoholic ammonia heated at 120° for several hours in a sealed tube with 3 : 4-dinitrodimethylaniline yields 4-nitro-3-aminodimethylaniline in yellow crystals, m. p. 135°. Similar treatment with an alcoholic solution of methylamine at 125° yields 4-nitro-3-methylaminodimethylaniline in yellow crystals, m. p. 115°. This compound crystallises with half a molecule of methyl alcohol in lustrous orange needles, m. p. 88–90°. When dimethylamine is similarly treated with 2 : 4-dinitrodimethylaniline, 4-nitrotetramethyl-*m*-phenylenediamine is formed in large, reddish-orange plates, m. p. 81°; 4-nitro-3-ethylaminodimethylaniline, orange needles, m. p. 98°; 4-nitro-3-aminodiethylaniline, clear, yellow crystals, m. p. 139°; 4-nitro-3-methylaminodiethylaniline, yellow crystals, m. p. 96–97°; 4-nitro-3-dimethylaminodiethylaniline, orange-yellow crystals, m. p. 63–64°, and 4-nitro-3-ethylaminodiethylaniline, pale yellow crystals, m. p. 78.5°, are all obtained by heating the appropriate amine with the appropriate dialkylaniline. J. F. S.

**Phenyltaurine and its Higher Homologues.** R. DEMARS (*Bull. Sci. Pharmacol.*, 1922, 29, 492–495; from *Chem. Zentr.*, 1923, i, 1019).—Phenyltaurine,  $NHPh \cdot CH_2 \cdot CH_2 \cdot SO_3H$ , is prepared by the action of aniline (2 mols.) on a mixture of chloroethanesulphonic acid (1 mol.) and aniline (1 mol.) at 130–140°. After repeated recrystallisation, large, dark brown crystals of the aniline salt are obtained. Hydrolysis by means of steam distillation yields the free acid. *N*-Phenylmethyltaurine,  $C_6H_5O_3NS$ , similarly prepared, forms violet crystals, m. p. 239–240°. *N*-Phenylethyltaurine,  $C_{10}H_{15}O_3NS$ , forms greenish-white crystals. *N*-Phenylmethyltaurine and *N*-phenylethyltaurine both dissolve cupric hydroxide (cf. Delépine and Demars, A., 1922, i, 923). G. W. R.

**Preparation of Condensation Products of the Aromatic Series containing Nitrogen and Sulphur.** LEOPOLD CASSELLA & Co., G. M. B. H. (D.R.-P. 367344 and 367345; from *Chem. Zentr.*, 1923, ii, 572).—Supplementary to numerous earlier patents. *N*-Acyl derivatives of *N*-monoalkylated aromatic amines, for example, *N*-acetylmethyl-*p*-toluidide,  $C_6H_4Me \cdot NMeAc$ , give with sulphur monochloride condensation products containing nitrogen and sulphur, with formation of the alkyl chloride and the corresponding acid (acetic acid). The compound obtained in the case

of *N*-acetylmethyl-*p*-toluidide is identical with that obtained by the action of sulphur monochloride on *p*-toluidine. G. W. R.

**Nitration of Aceto- $\beta$ -naphthalide.** V. VESELY and M. JAKŠ (Bull. Soc. chim., 1923, [iv], 33, 942—952).—When aceto- $\beta$ -naphthalide is nitrated in acetic acid solution, the nitro-group enters the nucleus first of all in the 1 or 8 position. The present authors have succeeded in isolating, in addition, a considerable proportion of 6-nitro-2-acetylaminonaphthalene, which forms clear yellow, felted needles, m. p. 224°. The corresponding 6-nitro- $\beta$ -naphthylamine crystallises from alcohol in clear orange flakes, m. p. 203°, and gives both a *normal* and an *acid sulphate*. 6-Nitro- $\beta$ -naphthal crystallises in yellow needles, m. p. 158°. Direct dinitration of aceto- $\beta$ -naphthalide gives, besides the 1:8-dinitro-compound, 1:5-dinitroaceto- $\beta$ -naphthalide, which crystallises from acetic acid in yellow needles, m. p. 200—201°. By the Gattermann reaction with copper powder and sodium nitrite on the diazonium sulphate of 6-nitro- $\beta$ -naphthylamine is obtained 2:6-dinitronaphthalene, crystallising in reddish plates, m. p. 268°. H. H.

**The Nitration of 1-Bromoaceto- $\beta$ -naphthalide.** VITĚZSLAV VESELY and KAREL DVOŘÁK (Chem. Listy, 1923, 17, 163—165).—Nitration with excess of cold nitric acid, *d* 1.525, of 1-bromoaceto- $\beta$ -naphthalide yields 1:8-dinitroaceto- $\beta$ -naphthalide, identical with the nitration product of 8-nitroaceto- $\beta$ -naphthalide. Using only sufficient nitric acid to form a mononitro-derivative, together with sulphuric acid, the chief product is a dinitrobromoacetonaphthalide, m. p. 250—251° (the position of the nitro-groups not being determined), together with a small quantity of 1-bromo-5-nitroaceto- $\beta$ -naphthalide, yellow, silky needles, m. p. 194°. In order to prove the orientation of this compound, it was prepared by the bromination of 5-nitroaceto- $\beta$ -naphthalide, and the products thus obtained were found to be identical. 1-Bromo-5-nitro- $\beta$ -naphthylamine, orange needles, m. p. 161—162°, is obtained by the hydrolysis of this substance. 1-Bromo-8-nitroaceto- $\beta$ -naphthalide, yellow needles, m. p. 180°, 1-bromo-4-nitroaceto- $\beta$ -naphthalide, lemon-yellow needles, m. p. 175—176°, and 1-bromo-6-nitroaceto- $\beta$ -naphthalide, yellow needles, m. p. 206—207°, were also prepared by the bromination of the corresponding nitroacetónaphthalides, the corresponding 1-bromonitronaphthylamines melting at 142—143°, 155°, and 222—223°, respectively. R. T.

**Preparation of 2-Hydroxy-1-arylaminonaphthalenes.** SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE SAINT DENIS, ANDRÉ WAHL, and ROBERT LANTZ (Brit. Pat. 182084, Fr. Pat. 548440, and D.R.-P. 365367; from Chem. Zentr., 1923, ii, 997—998).—Primary aromatic amines are allowed to react with 1-halogen- $\beta$ -naphthols. For example, 1-chloro- $\beta$ -naphthol is heated with aniline under a reflux apparatus. 1-Phenylamino- $\beta$ -naphthol thereby obtained forms needles, m. p. 153—154°, which become reddish-grey on exposure to air. By the action on it of methyl sulphate the corresponding methyl

ether is formed; prisms, m. p. 80.5°. *p*-Toluidine heated with 1-bromo- $\beta$ -naphthol at 125–130° yields 1-*p*-tolylamino- $\beta$ -naphthol, which forms crystals, m. p. 137–138°. G. W. R.

**The Chemistry of Naphthalene and its Derivatives. II. New Derivatives of Nitro- $\beta$ -naphthylamine.** N. N. VOROBYOV and K. A. GRIBOV (*Bull. Inst. Poly. Ivanovo-Voznesensk*, 1923, 7, 109–115).—The nitration of Brenner's acid ( $\beta$ -naphthylamine-6-sulphonic acid) leads to a good yield of 8-nitro- $\beta$ -naphthylamine-6-sulphonic acid which forms a light grey powder almost insoluble in water. It is characterised by the formation of orange ammonium and sodium salts; the colour of these salts is probably due to the auxochromic effect of the amino-group in the *amphiposition* to the salt-forming sulphonic group, whilst in the free acid these two groups probably form an internal salt. The structure assigned to the new acid is confirmed by its conversion into 1:3-nitronaphthalenesulphonic acid and the corresponding amino-acid and also 1:3-dichloronaphthalene. On reduction with iron and acetic acid, the nitro-acid passes into 2:8-naphthylenediamine- $\beta$ -sulphonic acid, an insoluble powder which can be tetrazotised and gives rise to substantive cotton dyes.

The nitration of amino-R-acid ( $\beta$ -naphthylamine-3:6-disulphonic acid) proceeds normally, but all attempts to isolate the nitration product lead to the partial or complete hydrolysis of the amino-group; the crude nitration product dyes wool and silk an intense brownish-yellow.

The nitration of amino-C-acid ( $\beta$ -naphthylamine-4:8-disulphonic acid) leads to the formation of the 6-nitro-derivative, which is also easily hydrolysed, but can nevertheless be isolated in the form of its sodium salt, which is a dark yellow powder; its structure follows from its conversion into 2:6-naphthylenediamine. The instability of this and the preceding compound is attributed to the effect of the sulphonic group attached to the ring carrying the amino-group. G. A. R. K.

**Catalytic Preparation of Aminocyclohexanols.** J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1923, 177, 158–160).—At 90° and 50 kg. pressure, *p*-nitrophenol (in alcoholic solution) absorbs hydrogen, in presence of nickel, producing *p*-aminophenol. At 180° and 60 kg. pressure, aminocyclohexanol is formed in an impure state. If, however, *p*-aminophenol is reduced at the higher temperature and pressure, the aminocyclohexanol is obtained as white crystals, with m. p. 64–65° and b. p. 235–245° (hydrochloride, m. p. 90°).

In the corresponding reduction of *o*-nitrophenol, an even less pure product is obtained, whereas, by reducing *o*-aminophenol, the aminocyclohexanol is obtained as white crystals, m. p. 47° and b. p. 220–240° (hydrochloride, m. p. 75°). Brunel (*A.*, 1903, i, 680) recorded for the three corresponding temperatures, 66°, 219°, and 175°, but whereas his cyclohexanol was an individual, that now obtained is a mixture of the *cis*- and *trans*-forms. E. E. T.

**Osmotic Pressures of Aqueous Solutions of Phenol at 30°.** ARTHUR GROLLMAN and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1923, **45**, 1705—1710).—The osmotic pressures of solutions of phenol have been determined throughout the solubility range at 30°. From the results so obtained the degree of association of phenol in aqueous solution has been calculated, and it is found that the percentage of simple molecules existing in the bimolecular condition varies from 86% in 0.1*M* solution to 99% in 0.9*M* solution. The pure material is entirely associated. It is suggested that the difference in the nature of the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentration is to be attributed to the different molecular combinations present. The great absorption of heat attending the dissolution of phenol in water is due to the partial dissociation of the higher molecular forms, the reaction  $(C_6H_5-OH)_2 \rightarrow 2C_6H_5-OH$  being endothermic. J. F. S.

**Preparation of Aryl Phosphates.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (EDUARD TSCHUNKUR and ERNST KNIEPEN) (D.R.-P. 367954; from *Chem. Zentr.*, 1923, ii, 915—916).—Aromatic cyclic or heterocyclic hydroxy-compounds or their substitution products are treated with phosphoryl halides in the presence of suitable catalysts, for example, magnesium, calcium, aluminium, their chlorides, or the chlorides of iron or chromium. The following compounds are prepared: *triphenyl phosphate*, from phenol and phosphorus oxychloride; *tri-p-tolyl phosphate*; *tri-β-naphthyl phosphate*, m. p. 110—111°; *resorcinyll phosphate*,  $(C_6H_4O)_3(PO)_2$  crystals, m. p. above 300°; *tri-8-quinolyl phosphate*, a granular substance, m. p. 175—176°; *phenyl-di-β-naphthyl phosphate*, a viscid mass solidifying on cooling, and having b. p. above 300°/9 mm. G. W. R.

**Chloral-*p*-acetylaminophenol.** O. HINSBERG (*Ber.*, 1923, **56**, [B], 1734).—The action of chloral on *p*-acetylaminophenol leads to the formation of a substance, (?)  $CCl_3-CH(OH)-O-C_6H_4-NHAc$ , a colourless, tasteless, crystalline solid, m. p. about 160° (decomp.) according to the rate of heating. It decomposes with evolution of chloral slowly at the atmospheric temperature, but rapidly when heated. The possibility that it is a molecular compound in which the components are united by subsidiary valencies is not excluded. H. W.

**The Action of Bromine on *p*-Hydroxy- and *p*-Methoxy-sulphonic Acids.** ANDREW NORMAN MELDRUM and MADHAVLAL SUKHLAL SHAH (*T.*, 1923, **123**, 1982—1986).

[The Isomerism of β-Naphthol Sulphides and the Analogous Isomerism of Aromatic *o*-Hydroxysulphides]. R. LESSEE and G. GAD (*Ber.*, 1923, **56**, [B], 1802; cf. this vol., i, 561). The failure of dehydrosulphides which contain a substituent in the ortho-position to the hydroxy-group to react with phenyl- or *p*-nitrophenyl-hydrazine is not necessarily a proof that they have the spiran constitution with a double thionylum ring. H. W.

**The Isomerism of  $\beta$ -Naphthyl Sulphide and its Derivatives.**

O. HINSBERG (*Ber.*, 1923, 56, [B], 1735—1736).—The author agrees with Lesser and Gad (this vol., i, 561), that the assumption of a peculiar sulphur isomerism is no longer necessary to explain the relationship of  $\beta$ -naphthyl sulphide and *iso*- $\beta$ -naphthyl sulphide. This is, however, not the case with certain of their derivatives, notably the corresponding sulphones and, in particular, the naphthathioxines (Nolan and Smiles, T., 1913, 103, 901). H. W.

**The Ternary Eutectic Point of the Three Systems: Resorcinol- $\alpha$ -Nitronaphthalene-Pyrocatechol; Quinol-Resorcinol-Pyrocatechol; Quinol- $\alpha$ -Nitronaphthalene-Pyrocatechol.** PIERRE SENDEN (*Bull. Soc. chim. Belg.*, 1923, 32, 281—285).—A continuation of work previously described (this vol., i, 461). Diagrams based on the experimental values obtained are given. The respective eutectic temperatures are 40.9°, 37.5°, and 48°. H. J. E.

**Alkali Metal as a Reagent for Weakened Valencies in Organic Compounds.** KARL ZIEGLER and FRITZ THIELMANN (*Ber.*, 1923, 56, [B], 1740—1745).—An alkali metal is very suitable for the detection of the presence of weakened valencies in widely-differing groups of organic compounds. Up to the present, this has been shown to be true for potassium and for the highly active alloy of sodium and potassium, but the action of metallic sodium has not been investigated.

$\alpha\gamma$ -Tetraphenylallyl ethyl ether, triphenylmethyl ethyl ether, phenyl triphenylmethyl ether, benzhydryl ethyl ether, dibenzhydryl ether, benzophenonedimethylacetal, and phenyl triphenylmethyl sulphide undergo fission in accordance with the scheme,  $R\cdot O\cdot R' + 2K = RK + K\cdot O\cdot R'$ , when shaken with potassium powder or with sodium-potassium alloy in the presence of anhydrous ethyl ether at the atmospheric temperature; the occurrence of the reaction under so mild experimental conditions is remarkable. The ethers are characterised by the presence of weakened valencies between the hydrocarbon radicles and the oxygen atom. Similar fission is unexpectedly observed with  $\alpha\alpha\beta\beta$ -tetraphenylethane and  $\alpha\alpha\alpha\beta$ -tetraphenylethane. Since the latter compounds are completely stable individuals which do not exhibit any tendency towards dissociation into radicles even at a much higher temperature than that used in these experiments, it is impossible to assume that the reaction with potassium is due primarily to a dissociation into radicles and subsequent union of the latter with the metal.

Triphenylmethyl peroxide when similarly treated yields the potassium derivative of triphenylcarbinol, fission occurring therefore between the oxygen atoms. H. W.

**Diphenylphenylacetylenylcarbinol,**  $CPh\equiv C-CPh_2-OH$ . CHARLES MOUREU, CHARLES DUFRAISSE, and COLIN MACKALL (*Bull. Soc. chim.*, 1923, [iv], 33, 934—942; cf. A., 1921, i, 35).—The substitution of the phenylacetylenyl group for one of the phenyl

groups of triphenylcarbinol does not markedly affect the alcoholic properties of the compound. Although attempts to prepare the benzoate and the acetate of the alcohol failed, the Grignard reagent reacts with it with evolution of gas. Phosphorus trihalides react with the alcohol to form the *chloride*, m. p. 70—71°, and the *bromide*, m. p. 72—73°. Attempts to prepare the ethyl ether were unsuccessful, a yellow substance, m. p. 87°, being obtained by the action of ethyl alcohol and sulphuric acid on diphenylphenylacetylenylcarbinol. This yellow substance may be brominated to give three products, of which two melt at 130—131° and 183—184°, respectively. The alcohol itself does not behave towards halogens as an acetylenic substance. Bromine and iodine attack it and its halides very slowly, and always with the evolution of hydrogen halide, in spite of the fact that all the hydrogen in the molecules of the halides is situated in the phenyl groups. No crystalline derivatives were isolated from the last reactions.

H. H.

**Application of the Strain Theory to the Ring System of Cholesterol.** A. WINDAUS and W. HÜCKEL (*Nachr. K. Ges. Wiss. Göttingen*, 1921, 162—183; from *Chem. Zentr.*, 1923, i, 850; cf. A., 1922, i, 658; this vol., i, 220).—The application of Blanc's reaction to the determination of the constitution of the polycyclic hydroaromatic acids formed from the degradation of cholesterol and the bile acids is discussed. It is shown that in the case of cholestanol contradictory results may be obtained. In the hydroaromatic systems examined, the rings are either in the *cis*- or *trans*-position to each other, according as the hydrogen atoms attached to the common carbon atoms lie on the same side or on opposite sides in the two rings. The rules which hold for the monocyclic systems are only applicable to *cis*-systems. With *trans*-systems different conditions obtain. From a study of models, the authors calculate the valency deflections for different systems. It is concluded that Blanc's reaction may be inapplicable to cholestanol. Whilst such exceptions are improbable for rings of three or four carbon atoms in complicated hydroaromatic compounds, the conditions are different for the 1:5- and 1:6-positions of the carbon atoms. With open chains and free rotation, the first and fifth (or sixth) carbon atoms approximate to the normal relative position of two carbon atoms. This is impossible with *trans*-ring systems, where ring closure is consequently difficult or impossible.

G. W. R.

**Relationships between Cholesterol and Bile Acids.** A. WINDAUS (*Z. angew. Chem.*, 1923, 36, 309—310).—The relationship of cholic acid, from ox galls, to cholesterol has already been established (A., 1920, i, 41), and it is probable that there is a genetic relationship between the two in the animal organism. The transformation of cholesterol into deoxycholic acid, one of the three specific acids of ox bile, for example, necessitates the replacement of an *isobutyl* group by a *carboxy*-group, the addition of water at the double bond, the spatial inversion of the asymmetric

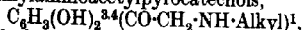
carbon atom 5 (annexed formula), and the removal of the hydroxyl group from carbon atom 4 to carbon atom 3. An investigation of the bile acid of the pig has now shown that the so-called  $\alpha$ -hyocholic acid has the formula  $C_{24}H_{40}O_4$ , not  $C_{25}H_{40}O_4$ , as in the literature. It is isomeric with deoxycholic acid and should be called hyodeoxycholic acid. It is a dihydroxycarboxylic acid, and gives on reduction hyocholanic acid, the decomposition product of cholanic acid. It has therefore the same configuration, as regards carbon atom 5, as cholesterol, and is more closely related to this than the deoxycholic acid from ox bile. The chenocholic acid from goose gall also contains twenty-four carbon atoms and can be transformed into cholanic acid.

E. H. R.

**Preparation of Nucleus-substituted Hydroxyl Derivatives of  $\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -arylethanes and  $\beta$ -Chloro- $\alpha$ -bisarylethanes.** OSCAR HINSBERG (D.R.-P. 364039; from *Chem. Zentr.*, 1923, ii, 912—913).—Monochloroacetal is allowed to react on phenol, substituted phenols, dihydroxyphenols, trihydroxyphenols, or naphthols in the presence of acids.  $\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -hydroxyphenylethane,  $OH \cdot C_6H_4 \cdot CH(OH) \cdot CH_2Cl$ , from phenol and chloroacetal in the presence of acetic acid and strong hydrochloric acid, is a powder with high m. p. which loses hydrogen chloride at  $130^\circ$ .  $\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -(4-hydroxy-2-methyl-3-isopropylphenyl)ethane, from chloroacetal and thymol, is a yellow, crystalline powder decomposing at  $160^\circ$  with evolution of hydrogen chloride. From chloroacetal (1 mol.) and thymol (2 mols.)  $\beta$ -chloro- $\alpha$ -bis(4-hydroxy-2-methyl-3-isopropylphenyl)ethane is obtained; it is crystalline.  $\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -di-*o*-hydroxyphenylethane, from chloroacetal and pyrocatechol, is a powder of high m. p., darkening on exposure to air.  $\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -trihydroxyphenylethane from pyrogallol and chloroacetal is a similar compound.  $\beta$ -Chloro- $\alpha$ -di-4-hydroxynaphthylethane, from chloroacetal and  $\beta$ -naphthol, forms small needles, m. p.  $174^\circ$ .

G. W. R.

**Preparation of Optically Active Aromatic Amino-alcohols.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92298 and Brit. Pat. 187129; from *Chem. Zentr.*, 1923, ii, 572).—Optically active salts of alkylaminoacetylpyrocatechols,



are reduced and the mixture of the salts of the optically active dihydroxyphenylethanol alkylamines, after separation of the amides, are changed into the free bases. For example, an aqueous solution of methylaminoacetylpyrocatechol (or ethylaminoacetylpyrocatechol) and *d*-tartaric acid is reduced by hydrogen in the presence of colloidal platinum. The platinum is precipitated and the solution, after its removal, concentrated. A crystalline by-product is removed and the filtrate evaporated to dryness. The

residue is then dissolved in methyl alcohol. After seeding with a crystal, *l-o-dihydroxyphenylethanolmethylethylamine-d-hydrogen tartrate* crystallises out whilst *d-o-dihydroxyphenylethanolmethylethylamine-d-hydrogen tartrate* remains in solution. The *l-o-dihydroxyphenylethanolmethylethylamine* obtained by the action of ammonia on an aqueous solution of the *d*-tartrate is identical with naturally prepared adrenaline. In the case of the corresponding derivatives of ethylamine, *d-o-dihydroxyphenylethanolmethylethylamine-d-hydrogen tartrate* crystallises out from the mixture of salts, whilst *l-o-dihydroxyphenylethanolmethylethylamine-d-hydrogen tartrate* remains in solution. *d-o-Dihydroxyphenylethanolmethylethylamine* has m. p. 197°. *l-o-Dihydroxyphenylethanolmethylethylamine* has also m. p. 197°. G. W. R.

**Preparation of an Optically Active Aromatic Amino alcohol.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92299; from *Chem. Zentr.*, 1923, ii, 572—573).—Racemic *o*-dihydroxyphenylethanolmethylethylamine is separated into the salt of its optically active isomerides by means of optically active  $\alpha$ -halogenocamphorsulphonic acids in the presence of suitable organic solvents. The free base is obtained from the salt of *l-o-dihydroxyphenylethanolmethylethylamine* by the usual methods. *l-o-Dihydroxyphenylethanolmethylethylamine-d- $\alpha$ -bromocamphorsulphonate* has m. p. 161° (decomp.) after discoloration at 155°. G. W. R.

**Trichloro-*tert*-butyl Nitrobenzoate.** T. B. ALDRICH (U.S. Pat. 1451357).—On being heated together, trichloro-*tert*-butyl alcohol and *m*-nitrobenzoyl chloride yield trichloro-*tert*-butyl *m*-nitrobenzoate, white plates, m. p. 86—88°.

CHEMICAL ABSTRACTS.

**Preparation of Urethane Derivatives of Benzoic Acid.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 93496 and 93750; from *Chem. Zentr.*, 1923, ii, 746).—*m*- or *p*-Amino benzoic acid is treated with ethylene chlorohydrin chloroformate and the chlorourethanebenzoic acid thereby formed allowed to react with primary aliphatic alcohols. The esters thus obtained are treated with diethylamine. By the action of ethylene chlorohydrin chloroformate on sodium *p*-aminobenzoate, *p*-chlorourethanebenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , is obtained as crystals. By the action of thionyl chloride, the corresponding acid chloride is obtained. This, by treatment with ethyl alcohol at 100°, gives ethyl chlorourethanebenzoate, a crystalline substance which with diethylamine at 100° gives ethyl diethylaminourethane-*p*-benzoate,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ . The free base has m. p. about 40°. The hydrochloride is crystalline and has m. p. 210° (decomp.). Alkyl diethylaminourethane-*m*-benzoate has m. p. about 50°. The hydrochloride forms crystals, m. p. 149—150°. G. W. R.

**Preparation of Urethane Derivatives of Benzoic Acid.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 94506 and 94983; from *Chem. Zentr.*, 1923, ii, 746; cf. preceding abstract).—Ethyl diethylaminourethane-*p*-benzoate may be prepared by

the action of ethyl *p*-aminobenzoate on ethylene chlorohydrin chloroformate and treatment of the urethane thereby obtained with diethylamine. By a similar reaction, *amyl diethylaminourethano-p-benzoate* is obtained. It has m. p. about 40°. The *hydrochloride* forms crystals, m. p. 138—139°. G. W. R.

**Preparation of Urethane Derivatives of Benzoic Acid.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 94569 and 94984; from *Chem. Zentr.*, 1923, ii, 746; cf. preceding abstracts).—Ethyl diethylaminourethano-*p*-benzoate may be prepared by reacting ethyl *p*-aminobenzoate with carbonyl chloride and allowing the ethyl phenylcarbamide-*p*-carboxylate (odourless crystals, m. p. about 60°) thereby obtained to react with diethylaminoethyl alcohol. Using dimethylaminoethyl alcohol, ethyl dimethylaminourethano-*p*-benzoate is obtained. Its *hydrochloride* is crystalline and has m. p. 224—225°. G. W. R.

**Preparation of Benzyl Esters of *p*-Dialkylaminomethylbenzoic Acids.** F. HOFFMANN-LA ROCHE & Co., AKT. GES. (Swiss Pats. 93500 and 93501; from *Chem. Zentr.*, 1923, ii, 573).—Benzyl esters of *o*-halogenomethylbenzoic acids are condensed with secondary aliphatic amines. By heating cyanobenzyl chloride with hydrobromic acid and warming the *p*-bromomethylbenzoic acid needles, m. p. 224°) thereby formed with thionyl chloride, *p*-bromomethylbenzoyl chloride is obtained. This gives with benzyl alcohol benzyl *p*-bromomethylbenzoate, m. p. 62°, which when heated with diethylamine, dimethylamine, or piperidine, respectively, at 100°, gives the following compounds. Benzyl *p*-diethylaminomethylbenzoate *hydrochloride*,  $C_6H_4(CO_2CH_2Ph)(CH_2NEt_2) \cdot HCl$ , crystals, b. p. 166°. Benzyl *p*-dimethylaminomethylbenzoate *hydrochloride*, colourless needles, m. p. 192°. Benzyl *p*-piperidinomethylbenzoate *hydrochloride*, leaflets, m. p. 183°. The products find use as local anaesthetics. G. W. R.

**Diacyl Derivatives of *o*-Hydroxybenzylamine.** L. CHAS. LAFORD and E. P. CLARK (*J. Amer. Chem. Soc.*, 1923, 45, 1738—1743).—It is shown that the benzoylation of *o*-hydroxybenzylacetamide does not cause migration of the acetyl radicle, and that the introduction of the acyl radicles in different orders gives isomeric acetyl-benzoyl derivatives. This is entirely different from the behaviour of such compounds in which both the reacting radicles are attached directly to the aromatic nucleus (A., 1922, i, 931). The action of boiling acetic anhydride on *o*-hydroxybenzylamine in the presence of concentrated sulphuric acid gives *o*-acetylbenzylacetamide, hexagonal plates, m. p. 102—103°, which is hydrolysed by means of cold aqueous alcoholic potassium hydroxide, with formation of *o*-hydroxybenzylacetamide; the latter gives the benzoate, m. p. 116° (cf. Auwers and Eisenlohr, who give m. p. 108—109°; *Annalen*, 1909, 369, 236), on benzoylation. The benzoate is reconverted into the *N*-acetyl derivative by hydrolysis by means of cold aqueous alcoholic potash. *o*-Acetylbenzylacetamide, needles, m. p. 85°, is obtained by the action of boiling

acetic anhydride and sodium acetate on *o*-hydroxybenzylbenzamide, into which it is reconverted by the action of cold alcoholic potassium hydroxide. The *N*-benzoyl derivative is obtained from the free base by benzoylation, but is more conveniently prepared by the hydrolysis by means of alcoholic potassium hydroxide of its benzoate, long, slender needles, m. p. 142—143°, which is produced from the free base by the action of benzoyl chloride and aqueous potassium hydroxide solution. W. S. N.

**Condensation of Nitriles with Thioamides. II. Acetonitrile with Thiobenzamide; and Benzonitrile with Thioacetamide.** SEIICHI ISHIKAWA (*J. Chem. Soc. Japan*, 1923, 44, 382—391; cf. A., 1921, i, 728).—Benziminoisothiobenzamide,  $\text{NH:CPh:N:CPh-SH}$ , was obtained by the condensation of benzonitrile and thiobenzamide. By passing dried hydrogen chloride into an ethereal solution of acetonitrile and thiobenzamide (A) or of benzonitrile and thioacetamide (B), the same condensation product, benziminoisothiobenzamide, is obtained, the yield being, however, poor. In the case of (A), thioacetamide is produced in the reacting solution, and in the case of (B) thiobenzamide was detected. A reversible reaction,  $\text{PhCN} + \text{NH:CMc-SH} \rightleftharpoons \text{NH:CPh-SH} + \text{MeCN}$ , has therefore occurred in the solution. The benzonitrile and thiobenzamide thus produced condense with one another. Two intermediate products,  $\text{NH:CMc:N:CPh-SH}$  and  $\text{NH:CPh:N:CMc-SH}$ , may be produced before the condensation, but were not isolated. K. K.

**The Action of Bases on  $\alpha\beta$ - and  $\alpha\beta\beta$ -Tribromo- $\beta$ -phenylpropionic Acids and their Esters.** P. RAMASWAMI AYYAR and J. J. SUBBOROUGH (*J. Ind. Inst. Science*, 1923, 6, 69—92).—In continuation of previous work on  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acids (T., 1903, 83, 666), a study has been made of the action of bases on  $\alpha\alpha\beta$ -tribromo- $\beta$ -phenylpropionic acid, and  $\alpha\beta\beta$ -tribromo- $\beta$ -phenylpropionic acid. On boiling the  $\alpha\alpha\beta$ -acid with water, carbon dioxide is split off almost quantitatively, the product being  $\alpha\beta$ -dibromostyrene. Alkali hydroxides in alcoholic solutions eliminate hydrobromic acid from both the tribromo-acids, yielding mixtures of the two stereoisomeric  $\alpha\beta$ -dibromocinnamic acids. With the  $\alpha\alpha\beta$ -acid or its ester, the ratio of *cis*- to *trans*-acid is 1 : 3.0, whilst with the  $\alpha\beta\beta$ -acid or ester the ratio is 1 : 1.4, but when much dibromostyrene is formed, the ratio may fall to 1 : 9 or even 1 : 12. In addition to the formation of the dibromocinnamic acids, dibromostyrene is also formed to some extent, favouring conditions being the replacement of alcohol by water, the use of dilute alkali, and high temperature. Hydrogen bromide is eliminated more readily from the  $\alpha\beta\beta$ -acid and its ester than from the  $\alpha\alpha\beta$ -acid or ester, and the  $\alpha\beta\beta$ -acid is also that which most readily loses carbon dioxide to give dibromostyrene. The tribromo-acids react with organic bases such as aniline, quinoline, and dimethylaniline, the chief reaction being elimination of carbon dioxide and hydrogen bromide, and formation of dibromostyrene, together with mixtures of (probably) mono- and di-bromocinnamic acids. With the esters, however, the main

reaction consists in elimination of bromine and production of *p*-bromodimethylaniline:  $\text{CHPh} \cdot \text{Br} \cdot \text{CBr}_2 \cdot \text{CO}_2\text{Me} + \text{NMe}_2\text{Ph} = \text{CHPh} \cdot \text{CBr} \cdot \text{CO}_2\text{Me} + \text{HBr} + \text{C}_6\text{H}_4\text{Br} \cdot \text{NMe}_2$  and  $\text{CPh} \cdot \text{Br}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{Me} + \text{NMe}_2\text{Ph} = \text{CBrPh} \cdot \text{CH} \cdot \text{CO}_2\text{Me} + \text{HBr} + \text{C}_6\text{H}_4\text{Br} \cdot \text{NMe}_2$ .

At the same time, hydrogen bromide is also eliminated to some extent, the product being therefore chiefly a mixture of mono- and di-bromocinnamic esters. This is of some interest, as the elimination of bromine from  $\alpha\beta$ -dibromo-compounds under the influence of bases is not usual (cf. T., 1922, 121, 1314). F. A. M.

**The so-called Distyrenic Acid of Fittig and Erdmann.** R. STÖRMER and WALTER BECKER (*Ber.*, 1923, 56, [B], 1440—1448).—Examination of "distyrenic acid" obtained by Fittig and Erdmann by the action of boiling sulphuric acid (50%) on cinnamic acid has shown that it is a mixture of substances which contains two saturated acids, for which the names distyranic and distyrenic acids are proposed, and unsaturated distyrenic acids from which a homogeneous material could not be isolated. Evidence is adduced to show that distyrenic acid is to be regarded as a 1:2-diphenylcyclobutane-3-carboxylic acid, whereas distyranic acid is probably a 1:3-diphenylcyclobutanecarboxylic acid, the constitution of which has not been completely elucidated owing to the difficult accessibility of the material.

The crude product of the action of sulphuric acid on cinnamic acid is purified from distyrene by treatment with alkali and ether and converted into the methyl esters by treatment with sodium hydroxide and methyl sulphate. The methyl esters are distilled in high vacuum, whereby mainly the saturated esters are volatilised whereas the unsaturated compounds cannot be removed without decomposition. The distillate is hydrolysed, giving mainly a mixture of saturated acids from which the removal of small quantities of unsaturated acid is effected only with great difficulty. The final mixture of saturated acids is separated by extraction with alcohol at 0° into *distyranic acid*,  $\text{C}_{17}\text{H}_{16}\text{O}_2$ , matted needles, m. p. 176°, and *distyrenic acid*,  $\text{C}_{17}\text{H}_{16}\text{O}_2$ , long, thin rodlets, m. p. 147°; the yield of the former compound is 0.3%, that of the latter 2.6% of the weight of the cinnamic acid used. Distyranic acid is converted into the corresponding *chloride*, a liquid which could not be caused to solidify, the *amide*, long, thin, colourless needles, m. p. 215°, the *anilide*, lustrous, slender needles, m. p. 194°, and the *methyl ester*, rhombic leaflets, m. p. 53°. The acid is not isomerised by pyridine at 160—170°; it is oxidised by permanganate to benzoic acid and a substance, m. p. 120°, which does not give the reactions of benzil. Distyrenic acid yields the corresponding *chloride*,  $\text{C}_{17}\text{H}_{15}\text{OCl}$ , a liquid which is very sensitive towards moisture, the *amide*, colourless, thin prisms, m. p. 205°, the *anilide*, colourless rodlets, m. p. 198°, and the *methyl ester*, long, thin rodlets, m. p. 72°, which regenerates the acid, m. p. 147°, when hydrolysed. The acid does not undergo isomerisation when treated with pyridine at 160—170°, with fuming hydrochloric acid at 150—160°, or when fused with potassium hydroxide. The *calcium*, *strontium*, *copper*, *zinc*, and *potassium*

salts have the unusual property of dissolving readily in chloroform, carbon disulphide, or acetone. Distyrenic acid is oxidised by potassium permanganate to benzoic acid and benzil. When calcium distyrenate is distilled with soda-lime, it yields  $\alpha\beta$ -diphenyl- $\Delta^2$ -butene,  $\text{CHPh:CPh}\cdot\text{CH}_2\cdot\text{CH}_3$ , m. p.  $56\cdot5^\circ$ .

The methyl esters which remain after distillation of the final mixture (see above) yield on hydrolysis an inseparable mixture of distyrenic acids. The impossibility of hydrogenating these acids by the customary methods and their inability to yield lactones appear to indicate the absence of  $\Delta^{\alpha\beta}$ - and  $\Delta^{\beta\gamma}$ -unsaturated acids, respectively. The original soft mass gradually passes into a hard, resinous material which appears to be a polyimide in which the carboxy-group takes part in the union of the individual molecules.

H. W.

**The Constitution of Sulphosalicylic Acid and of Related Substances.** ANDREW NORMAN MELDRUM and MADHAVLAL SUKHLAL SHAH (T., 1923, 123, 1986—1993).

**Preparation of New Carbonyl Derivatives of  $\alpha$ -Naphthol.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 181009; cf. U.S. Pat. 1387596).—Esters of  $\alpha$ -naphthol-4-carboxylic acid or of  $\alpha$ -naphthol-2:4-dicarboxylic acid, as well as of 4:4'-dihydroxy-1:1'-dinaphthyl ketone, are obtained, in addition to the dyes previously described (*loc. cit.*), by the interaction of  $\alpha$ -naphthol and a tetrahalogen derivative of methane, in the presence of a substance capable of neutralising an acid and of an aliphatic alcohol.

W. T. K. B.

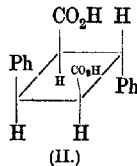
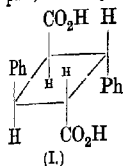
***o*-Quinones and 1:2-Diketones. VII. The Benzilic Acid Transformation in Cold Solution in the Absence of Air. The Cause of the Migration of the Radicle in the Benzilic Acid Transformation.** A. SCHÖNBERG and K. T. KELLER (*Ber.*, 1923, 56, [B], 1638—1642).—The production of benzoic acid during the benzilic acid transformation is due to atmospheric oxidation,  $\text{COPh}\cdot\text{COPh} + \text{O} + \text{H}_2\text{O} = 2\text{Ph}\cdot\text{CO}_2\text{H}$ . Its formation can be completely avoided by working in cold solution in the absence of air. The process has the further advantage that it is applicable to substituted benzils many of which do not yield benzilic acids under the usual conditions of the transformation. The presence of more than one molecular proportion of potassium alkoxide is not necessary for the conversion of benzil into benzilic acid; the intermediate compound is therefore the mono-derivative  $\text{OEt}\cdot\text{CPh}(\text{OK})\cdot\text{COPh}$ , and not the di-derivative. The cause of the transformation is sought in the tendency of the unequally loaded carbon atoms to equalise their valency demands.

Benzilic acid is conveniently prepared by the addition of a filtered solution of sodium hydroxide in alcohol (97%) to benzil dissolved in ether. The flask is filled to the neck, securely stoppered, and allowed to remain at the atmospheric temperature during twelve hours. The mixture is subsequently shaken with water, and benzilic acid is precipitated from the aqueous solution. 2:2'-Dimethoxybenzilic acid crystallises in colourless needles,

m. p. 160°. 4:4'-*Diethoxybenzilic acid*, colourless needles, m. p. 99°, and 3:3'-*dimethoxybenzilic acid*, colourless needles, m. p. 105°, are also described. H. W.

**The Molecular Configurations of Polynuclear Aromatic Compounds. IV. 6:6'-Dichlorodiphenic Acid; its Synthesis and Resolution into Optically Active Components.** GEORGE HALLATT CHRISTIE, CUTHBERT WILLIAM JAMES, and JAMES KENNER (T., 1923, 123, 1948—1951).

**The Stereochemistry of the Truxillic Acids. VII. R. STOERMER** [with CHRISTIAN WEGNER and ALFRED CARL] (*Ber.*, 1923, 56, [B], 1683—1695).—When a carboxyl group of the (five theoretically possible) truxillic acids is converted into the group CO-NHPh, the carbon atoms of the cyclobutane ring become, in part, actually asymmetric and hence certain of the anilic acids are



resolvable into their optical antipodes whereas others have the indivisible meso-configuration.  $\alpha$ - and  $\gamma$ -Truxillanic acids have been resolved into their optical antipodes; it is therefore possible to represent with certainty the configurations of  $\alpha$ - and  $\gamma$ -truxillic acid by the annexed formulæ, I and II.

The action of aniline on  $\alpha$ -truxillic anhydride leads to the formation of  $\alpha$ -truxillic acid,  $\alpha$ -truxillanic acid,  $C_{24}H_{21}O_4N$ , lustrous needles, m. p. 235°, and  $\alpha$ -truxillidaniide, m. p. 286°. *Methyl  $\alpha$ -truxillanilate*, prepared from the acid and methyl sulphate in alkaline solution, crystallises in slender needles, m. p. 173°, and the *ethyl ester* forms similar crystals, m. p. 151.5°. The acid is converted by thionyl chloride into  $\alpha$ -truxillanilyl chloride, almost colourless crystals, m. p. 168° (decomp.), which is transformed by aniline into the dianilide mentioned above and by dry ammonia into  $\alpha$ -truxillanilamide, m. p. 244°.

The resolution of  $\alpha$ -truxillanic acid into its optical antipodes is accomplished by means of strychnine in the presence of methylal. *Strychnine 1- $\alpha$ -truxillanilate* crystallises in aggregates of needles, m. p. 162° (decomp.). *1- $\alpha$ -Truxillanic acid*, slender needles, m. p. 205°, has  $[\alpha]_D^{20} = -23.0^\circ$ , when dissolved in acetone. *d- $\alpha$ -Truxillanic acid*, slender needles, m. p. 205°,  $[\alpha]_D^{20} +21.8^\circ$  in acetone, is obtained by the aid of brucine in methylal solution from the mixture of  $r$ - and  $d$ -acids isolated from the mother-liquors obtained during the resolution of the  $r$ -acid by strychnine. *Methyl 1- $\alpha$ -truxillanilate*, slender needles, m. p. 176°,  $[\alpha]_D^{20} -22.4^\circ$  in acetone and *ethyl d- $\alpha$ -truxillanilate*, m. p. 153°,  $[\alpha]_D^{20} +18.75^\circ$ , when dissolved in acetone, are also described. *d- $\alpha$ -Truxillanilyl chloride* has m. p. 135°,  $[\alpha]_D^{20} +12.42^\circ$  in acetone (the specimen was probably not perfectly homogeneous); it is converted by aniline into the optically inactive di-anilide, m. p. 286° (see above), whereas the levorotatory chloride is transformed by ammonia into *1- $\alpha$ -truxillanilamide*, m. p. 233°,  $[\alpha]_D^{20} -28.8^\circ$  in acetone. *r- $\alpha$ -Truxillidaniide* is hydrolysed by

k k\*

alcoholic potassium hydroxide solution only with extreme difficulty; the hydrolysed portion consists of a very difficultly separable mixture of  $\alpha$ - and  $\gamma$ -truxillanic acids. A similar mixture is obtained by heating the  $\alpha$ -anilic acid with alcoholic potassium hydroxide solution at  $120^\circ$ , whereas the conversion of  $\alpha$ - into  $\gamma$ -truxillic acid is never observed under these conditions.

$\alpha$ -Truxillic anhydride dissolved in benzene is converted by dry, gaseous ammonia into  $\alpha$ -truxilldiamide, m. p.  $267^\circ$ ,  $\alpha$ -truxillic acid and  $\alpha$ -truxillamic acid, slender, colourless needles, m. p.  $261^\circ$ ; the copper, manganese, nickel, and lead salts of the latter acid are insoluble in water, in which the alkali and alkali-earth salts dissolve readily. Attempts to resolve the acid by means of strychnine or brucine in the presence of methylal or alcohol were unsuccessful.  $\alpha$ -Truxilldiamide is highly stable towards alcoholic potassium hydroxide solution.

$\gamma$ -Truxillanic acid, small, matted needles, m. p.  $228^\circ$ , is conveniently prepared by the action of aniline on  $\gamma$ -truxillic anhydride in the presence of boiling alcohol; the methyl ester, slender, colourless needles, m. p.  $184.5^\circ$ ; the ethyl ester, slender needles, m. p.  $202^\circ$ , and the *n*-propyl ester, small, colourless needles, m. p.  $172^\circ$ , are described.  $\gamma$ -Truxillanilyl chloride, thick, colourless needles, m. p.  $156^\circ$ , prepared from the acid by means of thionyl chloride, but not by phosphorus pentachloride, is converted by dry, gaseous ammonia into  $\gamma$ -truxillanilamide, long, colourless needles, m. p.  $255^\circ$ , and by aniline into the dianilide, colourless needles, m. p.  $267.5^\circ$ .  $\gamma$ -Truxillanil,  $C_{16}H_{14} \begin{smallmatrix} \text{CO} \\ > \text{NPh} \end{smallmatrix}$ , leaflets, m. p.  $194^\circ$ , is

most conveniently prepared by heating  $\gamma$ -truxillanic acid with anhydrous sodium acetate and acetic anhydride at  $200^\circ$ ; it is indifferent towards aqueous potassium hydroxide solution but readily hydrolysed by the alcoholic reagent.

$\gamma$ -Truxillanic acid is resolved into its optical antipodes with unusual readiness by means of cinchonine in absolute ethyl-alcoholic solution. Cinchonine *d*- $\gamma$ -truxillanilate crystallises in slender needles, m. p.  $247^\circ$  (decomp.). *d*- $\gamma$ -Truxillanic acid, aggregates of slender needles, has m. p.  $228^\circ$ ,  $[\alpha]_D^{25} + 48.73^\circ$ , when dissolved in acetone. Cinchonine *l*- $\gamma$ -truxillanilate is an almost colourless, crystalline mass, m. p.  $112^\circ$  (decomp.). *l*- $\gamma$ -Truxillanic acid, slender needles, has m. p.  $228^\circ$ ,  $[\alpha]_D^{25} - 49.54^\circ$  in acetone. Methyl *l*- $\gamma$ -truxillanilate forms lustrous, woolly needles, m. p.  $202^\circ$ ,  $[\alpha]_D^{25} - 38.55^\circ$  in acetone. Ethyl *d*- $\gamma$ -truxillanilate, needles, m. p.  $206^\circ$ ,  $[\alpha]_D^{25} + 25.19^\circ$  in acetone; *l*- $\gamma$ -truxillanilyl chloride, lustrous needles, m. p.  $164^\circ$  (decomp.),  $[\alpha]_D^{25} - 9.53^\circ$  in acetone (which is converted by aniline into the *r*-dianilide, m. p.  $267.5^\circ$ ), and *d*- $\gamma$ -truxillanilamide, needles, m. p.  $253^\circ$ ,  $[\alpha]_D^{25} + 35.6^\circ$  in acetone, are also described.

H. W.

**Production of Imidothio-esters by the Condensation of Thiocarbimides with Resorcinol or Phloroglucinol.** R. J. KAUFMANN and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 1744—1752).—Alkyl- and aryl-thiocarbimides are condensed with

resorcinol or phloroglucinol in the presence of anhydrous ether, dry hydrogen chloride, and anhydrous zinc chloride, with production of the hydrochlorides of imidothio-esters,  $R\cdot C(SR')\cdot NH\cdot HCl$ . These substances are converted by boiling with water into the corresponding thio-esters,  $R\cdot CO\cdot SR'$ , which are converted by means of alkali into carboxylic acids,  $R\cdot CO_2H$ . The free imidothio-esters,  $R\cdot C(NH)SR'$ , are produced by the action of sodium hydrogen carbonate solution on the hydrochlorides; they readily react with alcohols, giving mercaptans and imido-esters,  $R\cdot C(NH)\cdot OR''$ , which, on boiling with dilute hydrochloric acid, pass, through the hydrochloride, into the esters,  $R\cdot CO_2R''$ , identical with the product formed from the carboxylic acids and the alcohol,  $R''OH$ .

These reactions have been conducted using methyl-, ethyl-, and benzyl-carbimides and *n*-butylcarbimide, which has b. p. 184.5—85.5°/743 mm.,  $d_4^{20}$  0.9563,  $n_D^{20}$  1.4636. In order to purify the imidothio-ester hydrochlorides, it is necessary to dissolve the crude product in cold hydrochloric acid and reprecipitate the free base, since much of the zinc in the crude product is present as the zinc salt of the condensation product. Such a zinc salt has actually been isolated from the experiment in which phenylthiocarbimide and resorcinol were used (see below). The condensations proceed much more slowly in the absence of zinc chloride, but the materials obtained are always much purer. The following compounds are described. *Methyl op-dihydroxythiobenzoate*, m. p. 97—98° (+ $H_2O$ , m. p. 70—71°), and its *di-p*-nitrobenzoate, m. p. 214—16°. *Methyl op-dihydroxyimidothiobenzoate*, white needles, m. p. 10°, and its *hydrochloride*, m. p. 224—226°. *S-Methyl op-dihydroxyimidothiobenzoate*, small, yellow needles, m. p. 197—199° (decomp.), *hydrochloride*, m. p. 244—245° (decomp.), *sulphate*, m. p. 30—231.5°. *Methyl-2:4:6-trihydroxythiobenzoate*, m. p. 190°. *Methyl-2:4:6-trihydroxyimidothiobenzoate*, m. p. 223—226°, *hydrochloride*, m. p. 255—256°. *Ethyl op-dihydroxybenzoate*, m. p. 70°, b. p. 170—176°/13—15 mm. *Ethyl op-dihydroxyimidothiobenzoate*, m. p. 214°. *Ethyl op-dihydroxythiobenzoate*, m. p. 60—1°, and its *di-p*-nitrobenzoate, m. p. 190—191°. *S-Ethyl op-dihydroxyimidothiobenzoate*, yellow crystals, m. p. 196—197° (decomp.), *hydrochloride*, m. p. 229.5—231.5° (decomp.), *sulphate*, m. p. 214—217°. *Butyl op-dihydroxythiobenzoate*, a light brown oil, gives a *di-p*-nitrobenzoate, m. p. 115—116°. *S-n-Butyl op-dihydroxyimidothiobenzoate*, bright yellow needles, m. p. 173—174° (decomp.), *hydrochloride*, m. p. 226—228° (decomp.). *S-Phenyl op-dihydroxyimidothiobenzoate*, yellow crystals, m. p. 156—158° (decomp.), *hydrochloride*, m. p. 220—222° (decomp.). This hydrochloride gives a zinc salt,  $C_{18}H_{10}O_2NClSZn$ , small, pale yellow crystals, m. p. 225—17° (decomp.).  
W. S. N.

**Phthalaldehyde.** L. SEEKLES (*Rec. trav. chim.*, 1923, 42, 6—709).—A method for the preparation of phthalaldehyde from naphthalene is described. Nine g. of naphthalene dissolved in 10 c.c. of dry ethyl acetate were treated with 160 litres of 9.6% ozonised oxygen, whereby the diozonide was produced. The solu-

tion was then shaken for twenty-four hours with 20 g. of ice and water and a little calcium carbonate and filtered. The yellow ethyl acetate solution of the aldehyde was separated from the aqueous layer and the latter extracted three times with ethyl acetate. The solution was dried over powdered fused sodium sulphate and the acetate distilled off at 40° in a vacuum. The orange-coloured syrup remaining was distilled in steam, when unchanged naphthalene and then phthalaldehyde passed over. The two distillates were collected separately. The aldehyde distillate was saturated with sodium sulphate and extracted twenty times with ethyl acetate. The extract was dried, the acetate removed in a vacuum at 40°, and the aldehyde crystallised from light petroleum. The aldehyde separated as short, hard, colourless crystals, m. p. 53.2, or as long, pale yellow needles, m. p. 56–57°. The residue in the flask from the steam distillation on keeping yielded colourless, hard plates which melted at 97° to a turbid liquid that cleared at 100° and is phthalaldehydic acid. From 18 g. of naphthalene, 8.5 g. of unchanged naphthalene were obtained, 1 g. of phthalaldehyde, and 8 g. of phthalaldehydic acid. The system phthalaldehyde–water has been investigated, and it is shown that a monohydrate exists, m. p. 45.3°. J. F. S.

#### The Beckmann Transformation of Oximinoketones.

SHINTARO KODAMA (*J. Chem. Soc. Japan*, 1923, 44, 339–352).—When oximinoacetophenone in combination with 2 or 3 mols. of sodium hydrogen sulphite,  $\text{COPh}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}\cdot 3\text{NaHSO}_3$ , is boiled with an equivalent amount, or excess, of 17–30% sulphuric acid for 1 minute, it is changed into an isomeride, colourless needles, m. p. 90–91°, which gives phenylglyoxylic acid when treated with an alkali hydroxide and is identical with the  $\alpha$ -isomeride of benzoylformamide,  $\text{COPh}\cdot\text{CO}\cdot\text{NH}_2$ , and can be changed into  $\beta$ - and  $\gamma$ -isomerides. This is a new example of the Beckmann transformation in the presence of water, the rearrangement having occurred in a case of dehydration. The reaction does not occur in the absence of the sulphite, and may be explained as follows:  
 $[\text{X}=\text{SO}_3\text{Na and Y}=\text{SO}_3\text{H}]\text{COPh}\cdot\text{CH}\cdot\text{NOH} \rightarrow \text{OH}\cdot\text{CPh}\cdot\text{X}\cdot\text{CHX}\cdot\text{NHX}$   
 $\rightarrow [\text{OH}\cdot\text{CPhY}\cdot\text{CHY}\cdot\text{NHY}] \rightarrow \text{COPh}\cdot\text{CO}\cdot\text{NH}_2$   
 K. K.

**Preparation of Tetrahydroxyquinone.** FÄRBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (BENNO HOMOLKA) (D.R.-PP. 368741 and 370222; from *Chem. Zentr.*, 1923, ii, 911).—Tetrahydroxyquinone is prepared by the action of alkali carbonates or magnesium oxide on glyoxal in the presence of atmospheric oxygen. Glyoxal may also be used in the form of its polymerides or as the sodium hydrogen sulphite compound. For example, glyoxal sodium hydrogen sulphite is added to an aqueous solution of sodium carbonate at about 50°. The solution absorbs oxygen, becomes yellow, and finally the *disodium* salt of tetrahydroxyquinone separates as bluish-black crystals with metallic green lustre. *Tetrahydroxyquinone* may be obtained from the sodium salt by treatment with hydrochloric acid. It forms large, lustrous, bluish-black crystals. G. W. E.

**Reduction Products of the Hydroxyanthraquinones. II.**  
JOHN HALL and ARTHUR GEORGE PERKIN (T., 1923, 123, 2029—2037).

**Derivatives of Anthraquinone. Reactions of Anthraquinone Sulphonic Acids with Mercaptans.** W. S. HOFFMAN and E. EMMET REID (J. Amer. Chem. Soc., 1923, 45, 1831—1838).—An extension of the previous research (A., 1922, i, 154). The following compounds are described:

1-Benzylthiolanthraquinone, m. p. 242°; 1:5-dibenzylthiolanthraquinone, dull orange, m. p. 176°; 1:8-dibenzylthiolanthraquinone, orange-red, m. p. 189°. 1-Benzylthiolanthraquinone-5-sulphonic acid and 1-benzylthiolanthraquinone-8-sulphonic acid as the sodium salts, with 2 and 3 molecules of water of hydration, respectively. 5-Benzylthiol-1-alkylthiolanthraquinones: *methyl*, m. p. 276°; *ethyl*, m. p. 208°; *propyl*, m. p. 210°; *butyl*, m. p. 235°; *isopropyl*, m. p. 239°; *isoamyl*, m. p. 211°. 8-Benzylthiol-1-alkylthiolanthraquinones: *methyl*, m. p. 262°; *ethyl*, m. p. 164°; *propyl*, m. p. 181°; *butyl*, m. p. 185°; *isopropyl*, m. p. 229°; *isoamyl*, m. p. 189°. These dithioethers are all orange to red in colour. 1-Benzylsulphoneanthraquinone, m. p. 233°; 1:8-dibenzyldisulphoneanthraquinone, m. p. 202°. Anthraquinone-5-benzyl-1-alkyldisulphones: *methyl*, m. p. 280°; *ethyl*, m. p. 210°; *propyl*, m. p. 215°; *butyl*, m. p. 228°; *isopropyl*, m. p. 229°; *isoamyl*, m. p. 202°. Anthraquinone-8-benzyl-1-alkyldisulphones: *methyl*, m. p. 255°; *ethyl*, m. p. 242.5°; *propyl*, m. p. 227°; *butyl*, m. p. 210°; *isoamyl*, m. p. 201°. 1-isoPropylthiolanthraquinone, gold coloured, m. p. 134°; 1:5-diisopropylthiolanthraquinone, orange, m. p. 148°; 1:8-diisopropylthiolanthraquinone, orange-red, m. p. 181°. Sodium 1-iso-propylthiolanthraquinone-5-sulphonate, +2H<sub>2</sub>O; sodium 1-isopropylthiolanthraquinone-8-sulphonate, +3H<sub>2</sub>O. 1-Alkylthiol-5-isopropylthiolanthraquinones: *methyl*, orange coloured, m. p. 184°; *ethyl*, gold coloured, m. p. 163°; *propyl*, gold coloured, m. p. 133°; *butyl*, orange-yellow, m. p. 114°; *isoamyl*, brown, m. p. 97°. 1-Alkylthiol-8-isopropylthiolanthraquinones: *methyl*, crimson, m. p. 189°; *ethyl*, crimson, m. p. 176°; *propyl*, orange-red, m. p. 135°; *butyl*, orange-red, m. p. 131°; *isoamyl*, orange-red, m. p. 109°. Anthraquinone-1-isopropylsulphone, m. p. 182°. Anthraquinonealkyl-5-isopropylsulphones: *methyl*, m. p. 235°; *ethyl*, m. p. 213°; *propyl*, m. p. 203°; *butyl*, m. p. 186°; *isopropyl*, m. p. 222°; *isoamyl*, m. p. 172°. 5-Butylthiolanthraquinone-1-alkylsulphones: *methyl*, *ethyl*, *propyl*, *butyl*, *isoamyl* have m. p., respectively, 256°, 210°, 204°, 162°, 189°. 8-Butylthiolanthraquinone-1-alkylsulphones: *methyl*, *ethyl*, *propyl*, *butyl*, *isoamyl* have m. p., respectively, 162°, 140°, 32°, 126°, 121°. These sulphone-thioethers and the preceding disulphones are yellow solids. The following compounds have been prepared with the aid of monothioethylene glycol: 1-β-hydroxyethylthiolanthraquinone, orange, m. p. 178°, its acetate, yellow, m. p. 146°; 1:5-di-β-hydroxyethylthiolanthraquinone, orange, m. p. 224°, diacetate, yellow, m. p. 199°; 1:8-di-β-hydroxyethylthiolanthraquinone, red, m. p. 206°, diacetate, m. p. 159°. A pure thioether

has not been obtained by the aid of ethylene mercaptan; but from this reagent and anthraquinonemonosulphonate a compound, m. p. above 250°, possibly  $S_2[(CH_2)_2S-C_{14}H_9O_2]_2$ , has been prepared. 1-Butylthiolanthraquinone-5-sulphonic acid is oxidised as the sodium salt by means of fuming nitric acid at 100° to sodium 1-butylsulphoneanthraquinone-5-sulphonate,  $+ \frac{1}{2}H_2O$ , from hot water,  $+ H_2O$  from cold water. This reacts extremely rapidly with mercaptans, giving the following 5-alkylthiolanthraquinone-1-butylsulphones: methyl, ethyl, propyl, butyl, isocamyl, having m. p., respectively, 228°, 214°, 201°, 162°, 152°, which give known disulphones (*loc. cit.*) on oxidation. The butylsulphone-sulphonate also reacts with thiophenol, giving a compound, m. p. above 350°, and with *p*-nitrothiophenol, giving an impure compound, m. p. above 300°. It is pointed out that the isopropyl thioethers may sometimes be oxidised to sulphones, but usually pass into sulphonic acids.

The formation of 1-butylsulphone-5-alkyl thioethers provides, it is claimed, a ready method for the identification of mercaptans.  
W. S. N.

**The Isomeric *l*-Menthyl Phenylchloroacetates.** ALEX. MCKENZIE and ISOBEL AGNES SMITH (T., 1923, 123, 1962—1978).

**New Halogen Derivatives of Camphor. III.  $\alpha'$ - and  $\alpha''$ -Dibromocamphor.** HENRY BURGESS and THOMAS MARTIN LOWRY (T., 1923, 123, 1867—1878).

**Investigations in the Camphor and Camphenilone Series.** S. NAMETKIN [with (FRL.) A. CHUCHRIKOFF, (FRL.) M. SCHLESINGER, and (FR.) L. BRÜSOFF] (*Annalen*, 1923, 432, 207—231).—A more detailed account of work already published (this vol., i, 586, 690), together with the following.

$\beta$ -Methylcamphenilone gives an *oxime*, long needles, m. p. 172°; a *hydrazone*, b. p. 245—247°/770 mm., m. p. 85—87°, and an *azine*,  $C_{10}H_{16} \cdot N \cdot N \cdot C_{10}H_{16}$ , rhombohedra, m. p. 163—164°. The hydrazone is converted by heating with sodium ethoxide at 180—200° into  $\beta$ -methylcamphenilane, m. p. 116—117°. The reduction of  $\beta$ -methylcamphenilone, by the action of sodium on its alcoholic solution, gives  $\beta$ -methylcamphenitol, a camphor-like substance, m. p. 172—173° (*phenylurethane*, needles, m. p. 104—105°, *hydrogen phthalate*, rhombs, m. p. 174—175°), which is partly dehydrated by means of phosphorus pentachloride, giving a *hydrocarbon*, b. p. 150—151°/744.5 mm.,  $d_4^{20}$  0.8546,  $n_D^{20}$  1.4589. The latter is probably a mixture; when it is oxidised by means of potassium permanganate, a small quantity of a solid remains, m. p. 110—112°, having an odour like that of a saturated bicyclic hydrocarbon. W. S. N.

**Reactions Differentiating Pinene from Nopinene. I. Permanganate Oxidation, Pinonic and Nopinic Acids.** G. DUPONT and G. BRUS (*Ann. Chim.*, 1923, [ix], 19, 186—198; cf. Dupont, A., 1922, i, 1042).—Oxidation of nopinene to pinonic acid by means of permanganate results in poor yields, so that the method is useless for estimation of the hydrocarbon. The acid obtained, however, is pure and of the active form. Similar treatment of

pinene results in a considerable amount of racemisation, the bulk of the product being inactive pinonic acid, although the amount racemised depends on the oxidation conditions. Yields of more than 50% of inactive pinonic acid were obtained by a method herein described, using inactive pinene as a starting point. The latter substance is prepared by optical neutralisation of *d*-pinene obtained in a pure condition from Aleppo turpentine with the *l*-isomeride from the Bordeaux product. [See *J.S.C.I.*, 1923, Sept.]

H. J. E.

**The Oxidation of Sabinene with Hydrogen Peroxide.**  
GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON (T., 1923, 123, 1849—1855).

**Extraction of Piperitone from Essential Oils.** JOHN READ and HENRY GEORGE SMITH (*J. Soc. Chem. Ind.*, 1923, 42, 339—340; cf. T., 1921, 119, 779; 1922, 121, 1863).—Details are given for the extraction of pure *dl*-piperitone from the essential oil of *Eucalyptus dives*. Extraction of the oil with normal sodium sulphite in a mechanically agitated, steam-jacketed vessel yields a crystalline compound from which feebly active piperitone can be regenerated by the addition of strong sodium hydroxide solution to its hot aqueous solution. Complete racemisation of the product so obtained may be effected by treatment with small quantities of alcoholic sodium hydroxide solution. For the isolation of specimens of the ketone of high rotatory power, recourse must be had to cautious fractional distillation of the essential oil under diminished pressure.

H. H.

**The Constituents of some Indian Essential Oils. IX. The Leaf Oil from *Pinus excelsa*. X. The Essential Oil from the Oleo-resin of *Pinus Gerardiana*, Wall.** JOHN LIONEL SIMONSEN (*Indian For. Rec.*, 1923, 9, 341—344, 345—348).—The pale yellow oil from *Pinus excelsa* (cf. this vol., i, 47), obtained by distillation in steam of the green cones and leaves, consists mainly of *l*- $\alpha$ -pinene and *l*- $\beta$ -pinene (about 84%), the higher boiling fractions containing limonene, *l*-terpineol, borneol, a sesquiterpene, and a sesquiterpene alcohol, the two latter substances being present in quantities insufficient for examination. The combined acids present are acetic, butyric or isobutyric, octoic and lauric (*l*, m. p. 43°) acids.

The oleo-resin from *Pinus Gerardiana* gives (per maund) 2.86 gallons of turpentine, and 66.8% of rosin. The former consists to the extent of about 80% of *d*- $\alpha$ -pinene (73%) and  $\beta$ -pinene, small quantities of a sesquiterpene (probably bicyclic, b. p. 157°/55 mm.,  $d_4^{20}$  0.9122,  $n_D^{20}$  1.4947,  $[\alpha]_D^{20}$  +24.08°; the yellow solution in acetic anhydride and a little sulphuric acid becomes emerald green and finally sage-green) and of a sesquiterpene alcohol also being present.

E. E. T.

**Action of Selenium Oxychloride on Pure Caoutchouc.**  
CARL E. FRICK (*J. Amer. Chem. Soc.*, 1923, 45, 1800—1804).—The action of selenium oxychloride, in ice-cold carbon tetrachloride solution, on synthetic caoutchouc from the polymerisation of

isoprene, or on the following natural *Hevea* rubbers, Pale Crepe, Smoked Sheet, Para, and Caucho Ball, leads to an amorphous powder, which is insoluble in the ordinary solvents for caoutchouc, and has lost its elasticity and swelling power. Slight differences in the composition of the product appear, depending on the source of the natural caoutchouc and the method of coagulation, but no essential difference can be detected between the behaviour of natural caoutchoucs and of the product synthesised from isoprene. This tends to support the view that their constitutions are essentially the same.

W. S. N.

**The Products of the Hydrolysis of Centaurein : Dextrose and Centaureidin.** BRIDEL and C. CHARAUX (*J. Pharm. Chim.*, 1923, [vii], 28, 5—13; cf. this vol., i, 122).—The sugar liberated by the hydrolysis of centaurein is shown, both by isolation and by the biochemical method of Bourquelot and Bridel (A., 1920, ii, 337), to be exclusively dextrose. An accurate estimation of the methoxyl groups in centaureidin by the Zeisel method is difficult, owing to the insolubility in hydriodic acid of the compound and its demethylation product, but the authors consider, from results obtained, that the molecule may contain three such groups and that the formula may thus be written  $C_{16}H_7O_8(OMe)_3$ .

W. T. K. B.

**Constitution of Cerebrin.** ALFONSO CRUTO (*Rassegna Clin. Terap. e Scienze Aff.*, 1922, 21, 257—259; from *Chem. Zentr.*, 1923, i, 1133).—Purified cerebrin has m. p. 182—183° and is free from ash. The fatty acid obtained from its hydrolysis with 3% sulphuric acid has m. p. 85—86° and is identical with hydroxyceerotic acid (Marie). Sphingosin, also obtained, agrees with that described by Thudichum and Thierfelder.

G. W. R.

**The Toxin of *Cicuta virosa*.** E. ŠVAGH (*Chem. Listy*, 1923, 17, 166—169).—No alkaloids are found in the rhizome of *Cicuta virosa*, and the substance, which has been named cicutine, and its glucoside do not therefore exist. The substances extracted from *C. virosa* are very readily oxidised by enzymes, yielding at least two resinous products, which still possess to a large extent the toxic properties of the extract. Two toxic substances are isolated, *cicutozin*, a yellow, amorphous acidic substance, slightly soluble in water, and forming a lead salt, and *cicutoxinin*, a neutral, less toxic substance. Cicutoxin exhibits absorption bands at  $\lambda$  570—640 and  $\lambda$  650—680.

R. T.

**Adsorbed Moisture and Water of Crystallisation in certain Common Dyes.** H. WALES and O. A. NELSON (*J. Amer. Chem. Soc.*, 1923, 45, 1657—1666).—Vapour pressure-composition curves have been constructed for methylene-blue, the zinc chloride compound of methylene-blue, crystal-violet, rosaniline hydrochloride, pararosaniline hydrochloride, erythrosine, and tartrazine for the purpose of ascertaining whether the water present in these dyes is adsorbed or is held as water of crystallisation. Crystal-violet and tartrazine alone furnish evidence of the existence of hydrates. In

the case of the former dye, the vapour-pressure curve at 26° indicates the existence of hydrates containing 9, 6, 4, 3, and 2 molecules of water, respectively, whilst tartrazine, which appears to form hydrates containing 14, 10, 6, and 3 molecules of water, apparently exists, after exposure to the air, as a hexahydrate. In the case of erythrosine, which is generally assumed to exist as a monohydrate, no indication of the existence of a hydrate could be found, but evidence is obtained that the equivalent of 1 molecule of water in erythrosine is present as part of the molecule and a new hypothesis of the structure of this compound is put forward.

J. F. S.

**The State of Methyl-orange and Methyl-red at the Transition Point.** A. THIEL and A. DASSLER (*Ber.*, 1923, 56, [B], 1667—1671).—The isoelectric points of these ampholytic indicators were determined by solubility methods and checked against indicators of known  $p_H$ . The isoelectric point of methyl-orange (the free acid) lies at  $p_H=1.7$ ; for methyl-red it lies at  $p_H=3.7$ . It is pointed out that both these indicators change into a deep red form in strongly acid solution. Formulæ are suggested to represent the various changes involved.

H. H.

**Furfurylidene- and Difurfurylidene-4-methylcyclohexanones.** (Mlle) N. WOLFF (*Compt. rend.*, 1923, 177, 197—199; cf. A., 1922, i, 668).—4-Methylcyclohexanone condenses with one molecule of furfuraldehyde in presence of sodamide to give 2-furfurylidene-4-methylcyclohexanone, pale yellow crystals, m. p. 43°, and with 2 molecules of furfuraldehyde, in presence of sodium methoxide, to give 2:6-difurfurylidene-4-methylcyclohexanone, yellow needles, m. p. 94°.

E. E. T.

**Sulphoacetic Acid as a Condensing Agent. V. Preparation of 2:4:6-Trimethylpyrylium Perchlorate from Mesityl Oxide.** WILHELM SCHNEIDER and ALFRED SACK (*Ber.*, 1923, 56, [B], 1786—1787).—2:4:6-Trimethylpyrylium perchlorate, m. p. 242° (decomp.), is more conveniently prepared from mesityl oxide, acetic anhydride, and sulphuric acid monohydrate than from 2:6-dimethylpyrone, according to the method of Baeyer and Piccard (*A.*, 1911, i, 901).

H. W.

**Flavonols and Anthocyanins.** KURT NOACK (*Z. Bot.*, 1922, 14, 1—74; from *Chem. Zentr.*, 1923, i, 964).—Flavonols occurring in the green parts of plants can be changed by reduction into anthocyanins. Formation of anthocyanin is associated with inhibition of assimilation or injury to chloroplasts. In normally assimilating cells, formation of anthocyanin from flavonols already present does not take place. In the system anthocyanin-flavonol, equilibrium is normally on the side of the flavonol. Anthocyanins are not attacked by emulsin. Cyanin, pelargonin, malvin, and chrysanthemin are readily decomposed by *Aspergillus* tannase into anthocyanidin and sugar. Mecocyanin is less readily decomposed, whilst violamin is unattacked. Flavonols are also decomposed by tannase. Cyanidine chloride, when heated with hydrochloric acid and a little formaldehyde, condenses to form a substance which is

similar to the tannin red obtainable from certain plant extracts which do not contain anthocyanins.  
G. W. R.

**Xanthyl Derivatives of Amino-acids.** R. FOSSE, PH. HAGÈNE, and R. DUBOIS (*Compt. rend.*, 1923, 177, 331—334).—Various compounds containing one or more amino-groups have been condensed with xanthhydrol; an amino-group condenses with the hydroxyl group of xanthhydrol, water being eliminated. Ethyl hydantoate with xanthhydrol gives *ethyl xanthylhydantoate*, needles, m. p. 201.5° (*potassium* salt described). Ethyl carbamidoisohexoate gives *ethyl xanthylcarbamidoisohexoate*, white crystals, m. p. 162—163°, whilst hydantoamide gives *xanthylhydantoamide*, m. p., according to speed of heating, 228° to 244°. *Hydantolylhydrazide* (m. p., according to speed of heating, 172° to 177°; obtained by the action of hydrazine on ethyl hydantoate) condenses with xanthhydrol to give *diraxanthylhydantolylhydrazide*, m. p., according to speed of heating, 206° to 217°.  
E. E. T.

**Xanthyllallantoin.** R. FOSSE and A. HIEULLE (*Compt. rend.*, 1923, 177, 199—202; cf. this vol., i, 860, and preceding abstract).—Xanthhydrol precipitates allantoin from very dilute solutions (diluted acetic acid) as *xanthyllallantoin*, condensation occurring between the hydroxyl and amino-groups in the two compounds respectively. The product cannot be confused with xanthylcarbamide. It melts at 214—215° (becoming coloured at 210°) and is soluble in boiling methyl alcohol. On grinding with normal potassium hydroxide and then diluting, it affords a solution from which acetic acid precipitates xanthyllallantoin. On keeping, or warming, the alkaline solution, *potassium xanthyllallantoate* separates. Hot concentrated hydrochloric acid converts xanthyllallantoin into the chloride of the hydrol and allantoin, which then undergoes hydrolysis.  
E. E. T.

**Preparation of Heterocyclic Compounds of the Naphthalene Series.** HERMANN STAUDINGER (Swiss Pats. 92688 and 93486—93489; from *Chem. Zentr.*, 1923, ii, 573).— $\beta$ -Naphthol,  $\beta$ -thionaphthol, or a  $\beta$ -*N*-monoalkylaminonaphthalene, monoaryalkylaminonaphthalene, or arylaminonaphthalene, is allowed to react with oxalyl chloride in the presence of diluents or condensing reagents such as carbon disulphide, benzene, aluminium chloride, or sulphuric acid. The diphenyldi-imidochloride of oxalic acid may be used in place of oxalyl chloride.  $\beta$ -Naphthol and oxalyl chloride give  $\beta$ -*naphthafuran-1:2-dione*, a yellow, crystalline powder, m. p. 183° (decomp.).  $\beta$ -Thionaphthol similarly gives  $\beta$ -*naphthathiofuran-1:2-dione*, a red crystalline powder, m. p. 153°.  $\beta$ -*Ethyl-naphthindole-1:2-dione*, from  $\beta$ -ethylaminonaphthalene and oxalyl chloride, is a red, crystalline powder, m. p. 174°.  $\beta$ -*Benzyl-naphthindole-1:2-dione*, has m. p. 185° and  $\beta$ -*phenyl-naphthindole-1:2-dione*, m. p. 227°, are red, crystalline powders.  
G. W. R.

**New Derivatives of Synthetic Adrenaline (Suprarenine).** CASIMIR FUNK and LOUIS FREEDMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1792—1795).—The action of boiling dry ethyl-alcoholic hydrogen

chloride on *r*-adrenaline hydrochloride gives the aliphatic ethyl ether, *r*- $\beta$ -3 : 4-dihydroxyphenyl- $\beta$ -ethoxyethylmethylamine hydrochloride, white crystals, m. p. 169°, in 65% yield, whilst with methylalcoholic hydrogen chloride the corresponding methyl ether, white, rectangular prisms, m. p. 175°, is produced in 26% yield. Both compounds give the same colour reactions. Addition of ferric chloride gives a dark green coloration, passing to maroon-red on keeping or addition of ammonia. An orange-red coloration is produced on addition of sodium acetate and mercuric chloride in aqueous solution. The free bases oxidise readily in the presence of alkali. During the preparation of the ethyl ether, diadrenaline ether hydrochloride,  $O(CH[C_6H_3(OH)_2] \cdot CH_2 \cdot NHMe, HCl)_2$ , thin, rectangular prisms, m. p. 180—183°, is formed as a by-product. It gives a deep green coloration with ferric chloride, changing to reddish-violet and violet on keeping, or addition of ammonia. With sodium acetate and mercuric chloride, a greyish-blue precipitate is formed, which darkens on keeping. With ammonia, a grey precipitate is formed, which dissolves in excess of ammonia, giving a purple solution. With phosphotungstic or phosphomolybdic acid, a greyish-white precipitate is formed.

W. S. N.

**Preparation of Acetyl Compounds of Quinine Aromatic Hydroxycarboxylates.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 365682; from *Chem. Zentr.*, 1923, ii, 916; cf. Merck, Diehl, and Mayen, A., 1922, i, 46).—Quinine aromatic hydroxycarboxylates are acetylated by the usual methods. Quinine *o*-acetoxybenzoate hydrochloride is prepared by the action of acetyl chloride on quinine salicylate. Quinine *o*-acetoxybenzoate is a light-coloured, resinous substance. By heating quinine 3-hydroxy-*m*-toluate (white platelets, m. p. 145°) with acetic anhydride, quinine 3-acetoxy-*m*-toluate is obtained; it forms small crystals, m. p. 169°.

G. W. R.

**Dimethiodides in the Eserine Series.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, 176, 1813—1815; cf. this vol., i, 700).—Attempts to obtain dimethiodides were successful with eseroline, eserethole, and eseretholemethine, but failed in the case of eserine itself. In no case is the fixation of the second mol. of methyl iodide complete. On the other hand, the dihydro-derivatives, especially those of the methine bases, give almost quantitative yields of stable dimethiodides. Dihydroeserinemethine dimethiodide,  $C_{16}H_{25}O_2N_3 \cdot 2MeI, H_2O$ , and dihydroeseretholemethine dimethiodide,  $C_{16}H_{25}ON_2 \cdot 2MeI, H_2O$ , are not attacked by dilute alkalis; hydrogenation has thus increased the basicity of the pyrrole nucleus. These substances were not obtained pure by the ordinary methods, but in presence of sodium ethoxide and excess of methyl iodide, crystalline products were formed. Eseroline yields an optically inactive dimethiodide, m. p. 235°; the same substance is obtained by using eserine or the methyl ester of eseroline as the starting point, thus indicating that the final product contains a methylated hydroxyl group. A further method of preparation is

from eseroline monomethiodide under similar conditions. This dimethiodide is apparently identical with that described by Stedman (T., 1921, 119, 891); the authors, however, assign to it the formula  $C_{19}H_{36}O_2N_2I_2$  or  $C_{19}H_{34}O_2N_2I_2$ . Eserethole yields an homologous dimethiodide, m. p. 207°, containing one more  $CH_2$  group, and eseretholemethine gives an identical derivative showing that in the process of exhaustive methylation intermediate formation of the methine base occurs with subsequent iodomethylation. H. J. E.

**The Alkaloids of the Calabar Bean. IX. The Nature of the Third Nitrogen Atom in Eserine.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1923, [iv], 33, 970—977).—This paper is mainly identical with that abstracted in this vol., i, 700.  $\alpha$ -Eseretholemethine methiodide is now stated to have m. p. 140—141°. By reduction with zinc and hydrochloric acid, etheseroline gives hydroetheseroline, a neutral oil with  $\alpha_D - 30^\circ$  in 95% alcohol,  $c = 0.07$ ; this gives a methiodide with  $\alpha_D - 20^\circ$  in water. H. H.

**The Alkaloids of the Calabar Bean. X. The Di-acid Nature of Eserine Derivatives. Dimethiodides.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1923, [iv], 33, 977—988; cf. preceding abstracts and T., 1923, 123, 758).—The fact that eserine, eseroline, eserethole, and eseretholemethine do not form dimethiodides, although they contain two basic nitrogen atoms in the molecule, is explained by the insolubility in methyl iodide of the monomethiodides first formed. By working in methyl-alcoholic solution, it is possible to increase the absorption of methyl iodide and to obtain products corresponding with mixtures of mono- and dimethiodides. The dihydro-derivatives of these compounds, on the other hand, form stable dimethiodides with ease. If methylation is carried out in a sealed tube in the presence of sodium ethoxide, it is found that eserine and its derivatives give dimethiodides, and, in addition, add on two methyl groups and one hydroxyl group. Thus, dihydroeseroline, dihydroeserine, or their methine bases, all give a dimethiodide which crystallises in colourless needles, m. p. 205°. H. H.

**Preparation of Keto Derivatives of the Morphine Series.** KNOLL & Co. (D.R.-P. 365683; from *Chem. Zentr.*, 1923, ii, 916—917).—Morphine or its alkyl ethers are hydrogenated in the presence of acids and comparatively large quantities of catalysts such as palladium or platinum or their salts. The reaction consists in simultaneous hydrogenation and rearrangement of the alcoholic hydroxyl group to form a keto group. The morphine keto base of composition  $C_{17}H_{19}O_3N$  has m. p. 262—263°. With hydroxylamine sulphate, it gives an oxime which forms crystals having m. p. above 234°. The semicarbazone has m. p. above 250°. By methylation of the morphine keto base, the codeine keto base,  $C_{18}H_{21}O_3N$ , is obtained; it has m. p. 193—194°; the oxime has m. p. 265—266°; the semicarbazone has m. p. 247—248°; and the methiodide, m. p. 273°. The bases give salts with acids such as diethylbarbituric acid and diallylbarbituric acid. G. W. R.

**Preparation of Halogenoethyl Morphines.** GEORG VON KERESZTY and EMIL WOLF (Aust. Pat. 88673; from *Chem. Zentr.*, 1923, ii, 809).—Morphine and alkali alkylloxides are treated with halogenoethyl esters of an arylsulphonic acid. For example, a solution of morphine in ethyl-alcoholic sodium ethoxide is added slowly at 20–25° with shaking to an ethyl-alcoholic solution of chloroethyl benzenesulphonate. *Chloroethylmorphine* has m. p. 75°. At higher temperatures it solidifies and has a second m. p. 105°. The *hydrochloride* is crystalline and has m. p. 150–151°.

G. W. R.

**Strychnos Alkaloids. XXXIX. The Violet Sulphite from Cacotheline and other Derivatives Thereof.** HERMANN LEUCHS and WALTER HEMPEL (*Ber.*, 1923, 56, [B], 1775–1780).—Cacotheline,  $C_{21}H_{21}O_7N_3 \cdot HNO_3$ , is converted by aqueous sodium sulphite under definite conditions into a *nitroquinol sulphite*,  $C_{21}H_{21}O_7N_3 \cdot H_2SO_3$ , dark violet platelets. The presence of a carboxyl group is proved by the formation of a *monomethyl ester*,  $C_{23}H_{25}O_{10}N_3S$ , bluish-violet prisms. The violet sulphite is oxidised by ferric chloride to a *nitroquinone sulphite*,  $C_{21}H_{21}O_{10}N_3S$ , which is reconverted into the initial material by sulphurous acid. The nitroquinone is reduced by tin and hydrochloric acid to the *sulphite* of the *aminoquinol*,  $C_{21}H_{23}O_7N_3S$ , prisms (corresponding *hydrochloride*, colourless prisms or needles). Oxidation of the violet sulphite dissolved in ammonia by means of air leads to the formation of the *oxide* of the *nitroquinol sulphite*,  $C_{21}H_{21}O_{11}N_3S$ , yellowish-brown plates, which is transformed by methyl alcohol and sulphuric acid into a *substance*,  $C_{23}H_{27}O_{13}N_3S$ , colourless, thin prisms or pale yellow, quadratic plates or domatic prisms, the formation of which appears to be due to the esterification of the carboxy-group and

conversion of the group  $\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{O} \end{array} \text{C}$  into  $\text{C}(\text{OH})\text{C}(\text{OMe})$ ; it is converted by potassium hydrogen carbonate solution into the *monomethyl* compound,  $C_{22}H_{25}O_{12}N_3S$ , colourless, rectangular prisms or long needles.

The following substances have not been described previously. The *diethyl ester* of the nitroquinol of the cacotheline base,  $C_{25}H_{31}O_7N_3$ , reddish-violet needles, m. p. 182°, which is oxidised by air to the *monoethyl ester* of the quinone, small, yellow prisms, which become discoloured, but do not melt above 180°; the *dimethyl ester* of the nitroquinol, reddish-violet prisms, m. p. 211° (decomp.) after softening at 170°, and the *monomethyl ester* of the cacotheline base,  $C_{23}H_{23}O_7N_3$ , dark yellow needles; the *methosulphate* of the nitroquinol dimethyl ester,  $C_{25}H_{33}O_{11}N_3S$ , violet needles and the corresponding *methiodide*,  $C_{25}H_{30}O_{11}N_3I$ , dark violet needles, and *methochloride*,  $C_{24}H_{30}O_7N_3Cl$ , reddish-violet needles.

H. W.

**Strychnos Alkaloids. XL. Esterification of Brucinonic and Related Acids.** HERMANN LEUCHS and WERNER GLADKORN (*Ber.*, 1923, 56, [B], 1780–1785).—During the oxidation of brucine to brucinonic acid it has been assumed (A., 1908, i, 563) that a

group,  $-\text{CH}:\text{CH}-$ , is transformed into two carboxyl groups one of which is free whereas the other is neutralised within the molecule. Further attempts to prove the presence of the second carboxyl group are now described.

The crystalline lead salt, when prepared according to different methods, is derived invariably from the monobasic acid.

Brucinonic acid is converted by treatment with methyl alcohol and hydrogen chloride into *methyl brucinonate*,  $\text{C}_{24}\text{H}_{27}\text{O}_8\text{N}_3$ , long prisms, m. p. 221–224°, and further apparently into the dimethyl ester the amorphous chloroplatinate of which gives analytical results approximating to those required by a derivative of the dimethyl ester hydrate. The oxime of brucinonic acid, on the other hand, gives a *monomethyl ester*,  $\text{C}_{24}\text{H}_{27}\text{O}_8\text{N}_3$ , hexagonal leaflets, m. p. 265° (decomp.),  $[\alpha]_D^{25} + 81.7^\circ$  in glacial acetic acid solution (a hydrated form, needles, is also described) and a *dimethyl ester hydrate*,  $\text{C}_{25}\text{H}_{31}\text{O}_9\text{N}_3$ , short prisms, m. p. 144–146° after softening at 140° (*hydrochloride*,  $\text{C}_{25}\text{H}_{31}\text{O}_9\text{N}_3\text{HCl}$ , colourless, rectangular leaflets; *methiodide*,  $\text{C}_{25}\text{H}_{34}\text{O}_9\text{N}_3\text{I}$ , colourless leaflets or oblique prisms, m. p. 185–187° [decomp.] after softening at 175°); the possibility that the group  $\text{N}\cdot\text{CO}\cdot$  is converted into  $\text{NH}/\text{CO}\cdot\text{H}$ , with the formation of a new carboxyl group, renders the demonstration of the presence of the original second carboxyl group uncertain. The *ethyl ester* of brucinonic acid oxime,  $\text{C}_{25}\text{H}_{29}\text{O}_8\text{N}_3$ , crystallises in long, thin prisms, m. p. about 280° (decomp.) after darkening at 260°. The monomethyl ester is transformed by hydrazine hydrate into the *hydrazide* of brucinonic acid oxime,  $\text{C}_{22}\text{H}_{27}\text{O}_7\text{N}_5$ , lustrous leaflets, m. p. about 265° (decomp.) after darkening at 245°, which is converted by sodium nitrite into the corresponding *azide*; the latter substance when treated with water at 100° gives nitrogen, formaldehyde, and a neutral compound,  $\text{C}_{23}\text{H}_{29}\text{O}_6\text{N}_3$ , lustrous needles which soften without melting at 210–220°.

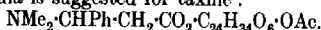
Dihydrobrucinonic acid is converted by gentle esterification into the corresponding *monoethyl ester*,  $\text{C}_{25}\text{H}_{30}\text{O}_8\text{N}_3$ , prisms, m. p. 227–229°, and *methyl ester*,  $\text{C}_{24}\text{H}_{28}\text{O}_8\text{N}_3$ , short prisms, m. p. 223–224° (a hydrated form is also described). More energetic treatment of the acid with methyl-alcoholic hydrogen chloride gives dimethyl brucinonate hydrate, which is characterised by the crystalline *methiodide*,  $\text{C}_{26}\text{H}_{35}\text{O}_9\text{N}_3\text{I}$ , colourless, domatic prisms, m. p. about 165° (decomp.), and the *hydrochloride*,  $\text{C}_{26}\text{H}_{32}\text{O}_9\text{N}_3\text{HCl}$ , transparent plates, m. p. 175–176° (decomp.).

Brucinolic acid is transformed similarly into the *monoethyl ester*,  $\text{C}_{25}\text{H}_{30}\text{O}_8\text{N}_3$ , colourless, rectangular leaflets, m. p. 121–123° (which is converted by alcoholic hydrogen chloride into brucinolone-*b*) and the *monomethyl ester*,  $\text{C}_{24}\text{H}_{28}\text{O}_8\text{N}_3$ , hexagonal plates, m. p. 205–207° after softening at 200°. The *methiodide* of *dimethyl brucinolate hydrate*,  $\text{C}_{26}\text{H}_{35}\text{O}_9\text{N}_3\text{I}$ , small leaflets, has m. p. 140–144° (decomp.) after much softening at 128°. H. W.

**Taxine.** II. E. WINTERSTEIN and A. GUYER (*Z. physiol. Chem.*, 1923, 128, 175–229; cf. A., 1922, i, 572).—The quantity of taxine which may be extracted from the yew, *Taxus baccata*, is

apparently independent of the locality in which the tree is grown, although male trees contain on the average about twice the amount present in female trees. The boughs and young sprouts contain a very small amount.

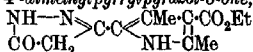
It has not yet been possible to obtain taxine,  $C_{37}H_{51}O_{10}N$ , in a crystalline condition. When distilled, it yields a small quantity of cinnamic acid, and on distillation with zinc dust styrene is obtained and when oxidised, benzoic acid, formaldehyde, cinnamic acid, acetic and oxalic acids are formed. Nitric oxide passed into an ethereal solution of taxine produces a mixture of the nitrate and the nitrite. When methylated with methyl iodide, a methiodide,  $C_{37}H_{51}O_{10}N, MeI$ , is formed, m. p. 123—125°; it is a rather unstable product which could not be obtained crystalline. When treated with water, or, better, with sodium hydroxide solution, this methiodide decomposes, forming trimethylamine and an amorphous compound of the formula  $C_{35}H_{44}O_{10}$ , a white powder, m. p. 120—140°, which on distillation or on treatment with acid yields cinnamic acid, and on oxidation with permanganate, benzaldehyde and benzoic acid, whilst by the action of sodium hydroxide solution in the cold, acetic and cinnamic acids and an insoluble product are formed. Taxine itself, when treated with sodium hydroxide solution, yields 1 molecule of acetic acid, a little cinnamic acid, and a basic amorphous compound containing nitrogen. If this compound, or taxine, is heated on the water-bath with 5% sulphuric acid for ten hours, a crystalline compound,  $C_{11}H_{15}O_2N$ , is obtained; hydrochloride,  $C_{11}H_{15}O_2N \cdot HCl$ , m. p. 173—174° (decomp.); hydrobromide, needles, m. p. 183°; chloroaurate, yellow needles, m. p. 135—136°; chloroplatinate, m. p. 208—210°. This compound, compact, spear-shaped crystals, yields, when heated, cinnamic acid and trimethylamine, and when oxidised benzoic acid and benzaldehyde and is probably  $\beta$ -dimethylamino- $\beta$ -phenylpropionic acid. The following formula is suggested for taxine:



Substances different from those obtained by chemical means are produced from taxine by bacteria. The physiological properties of taxine have been further investigated. W. O. K.

**Some Derivatives of Pyrrole.** H. FISCHER and K. SCHNELLER (*Z. physiol. Chem.*, 1923, 128, 240—253).—3-Acetyl-2:4-dimethylpyrrole reacts with chloroacetonitrile in ethereal solution in presence of hydrogen chloride to yield an imino-compound, which when treated with water yields 3-acetyl-5-chloroacetyl-2:4-dimethylpyrrole, colourless leaflets with a silky lustre, m. p. 173°. This compound, when treated with alcoholic ammonia, is converted into 3-acetyl-5-aminoacetyl-2:4-dimethylpyrrole, yellow crystals, which decomposes without melting, and when treated with alcoholic dimethylamine, is converted into 3-acetyl-5-dimethylaminoacetyl-2:4-dimethylpyrrole, fine needles, m. p. 104°. Similarly, ethyl 2:5-dimethylpyrrole-3-carboxylate condenses with dichloroacetonitrile to yield ethyl 4-dichloroacetyl-2:5-dimethylpyrrole-3-carboxylate, fine, white needles, m. p. 171°, and with methyl cyanoacetate to yield

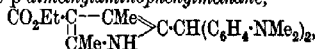
*methyl 3-carbethoxy-2:4-dimethylpyrrole-5-acetate*,  $C_{13}H_{17}O_4N$ , silky needles, m. p.  $124^\circ$ , whilst with cyanoacetic acid a similar condensation takes place, but carbon dioxide is evolved and ethyl 5-acetyl-2:4-dimethylpyrrole-3-carboxylate is formed. From carbonyl chloride and ethyl 2:4-dimethylpyrrole-3-carboxylate in toluene solution, 3-carbethoxy-2:4-dimethylpyrrole-5-carboxyl chloride, colourless leaflets, m. p.  $192^\circ$ , is obtained. If ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-acetate is warmed with hydrazine hydrate, 3-3'-carbethoxy-2':4'-dimethylpyrrolpyrazol-5-one,



is formed, fine, silky, colourless needles, m. p.  $268^\circ$ .

If the imino-hydrochloride from ethyl 5-benzoyl-2:4-dimethylpyrrole-3-carboxylate is heated in alcoholic solution and freshly prepared sodium amalgam added, *phenylbis-3-carbethoxy-2:4-dimethylpyrrolmethane*,  $\text{CHPh} \left( \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{NH} \cdot \text{CMe} \end{array} \right)_2$ , is formed, colourless leaflets turning red in the air, m. p.  $182^\circ$ .

Diazotised benzidine condenses with ethyl 2:4-dimethylpyrrole-3-carboxylate to yield an orange-red dye, m. p.  $239^\circ$ , and with 3-acetyl-2:4-dimethylpyrrole to yield a light orange dye, m. p.  $298^\circ$ . Tetramethyl-*pp*-diaminobenzhydrol condenses on the boiling water-bath in presence of potassium hydrogen sulphite with ethyl 2:4-dimethylpyrrole-3-carboxylate to form 3-carbethoxy-2:4-dimethylpyrrolbis-*p*-dimethylaminophenylmethane,



colourless leaflets from alcohol, m. p.  $176^\circ$ , and with ethyl 2:5-dimethylpyrrole-3-carboxylate, and with 3-acetyl-2:4-dimethylpyrrole to form similar compounds, m. p.  $142^\circ$  and  $165^\circ$ , respectively.

An attempt to prepare  $\beta$ -acetic- $\beta'$ -methyl maleic anhydride by the condensation of acetylsuccinic acid and potassium cyanide did not lead to the desired result. Instead, carbon dioxide was eliminated and dimethylmaleic anhydride was formed. W. O. K.

**Some Pyridine Derivatives of Iridium. II. MARCEL DÉLÉPINE** (*Ann. Chim.*, 1923, [ix], 19, 145—179; cf. this vol., i, 480).—Potassium iridotetrachloro-oxalate, prepared according to Vélez and Duffour's method (A., 1909, i, 762), experimental details of which are given, was used as a starting-point for new substitutions. Difficulties were experienced in preparing potassium *trans*-iridodichlorodioxalate, and investigation showed that this substance is always formed as a by-product in the preparation of the *cis*-isomeride, whilst it may also be obtained by intramolecular transformation of that substance. Experiment showed that, in the former case, each of the two isomerides is formed directly, no subsequent transformation taking place. The *cis*- may be converted into the *trans*-form by heating at  $130^\circ$  for one hour in the presence of potassium chloride, but the proportion of the substance which undergoes the change is small. The product, potassium *trans*-iridodichlorodioxalate,  $\text{K}_2\text{IrCl}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , forms either large, ruby-red, monoclinic

needles, or flattened, triclinic prisms. Both crystalline forms are hydrated to the same extent; the monoclinic crystals are deposited at temperatures above  $40^{\circ}$ , and in solution this form appears to be converted into the triclinic variety at about  $30^{\circ}$ . In the solid state, however, it is stable at the ordinary temperature. Although the *cis*- and *trans*-isomerides are similar in colour, the former possesses in solution twice the colour intensity of the latter for equal concentrations. Solutions of the two substances, which are equal in depth of colour, exhibit identical absorption spectra. The change from *cis*- to *trans*-configuration is reciprocal, but only takes place slowly in either direction. The resolution of the *cis*-isomeride into its optically active components was effected by means of the strychnine salts. Solutions of the separated components were kept for three years, when the *laevo*-form was found to have maintained its activity in full, whilst that of the *dextro*-form had somewhat diminished. This is considered to indicate the great stability of the molecule built up on a central iridium atom. Potassium *trans*-dioxalodipyridineiridiate forms sulphur-yellow, octahedral crystals containing at least  $6\text{H}_2\text{O}$ , which rapidly effloresce, becoming yellowish-white and opaque. From hot concentrated solutions, crystals containing  $2\text{H}_2\text{O}$  are deposited in the form of characteristic monoclinic needles. This substance may be transformed into the red tetrachlorodipyridine compound by the action of aqua regia, whilst with hydrochloric acid it yields a mixture of (a) two slightly soluble and (b) four readily soluble substances. The former consist of *iridium aquochlorodipyridine oxalate*,  $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})\text{Cl}(\text{C}_2\text{O}_4)$ , pale chamois-yellow needles, and *iridium diaquodichlorodipyridine dipyridinotetrachloride*,  $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4][\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ , rosy, orange crystals, which are hydrolysed by boiling water and converted by ammonia into ammonium dipyridinotetrachloroiridate and dichloroaquodipyridineiridic hydroxide. The latter include iridodichlorodiaquodipyridine chloride and potassium hydrogen oxalate, with traces of potassium pentachloropyridineiridate and pyridine hydrochloride. In a discussion of the mechanism of this reaction with hydrochloric acid, the author draws the conclusion that the pyridine groups are highly resistant to attack, and are not changed in position in the series of reactions involved.

The entry of a third molecule of pyridine into iridium dipyridinotetrachloride is only effected after heating for four hours at  $130^{\circ}$  in a sealed tube. *Iridium 1 : 2 : 6-tripyridinotrichloride*,  $\text{Ir}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3$ , yellow crystals, may be separated from its isomeride *iridium 1 : 2 : 3-tripyridinotrichloride*, yellow needles, which is formed simultaneously, by fractionation with chloroform, in which the former is considerably more soluble.

A general discussion of the application of Werner's co-ordination theory to the author's work is appended.

H. J. E.

**The Action of Benzaldehydes on Free *o*-Aminophenylacetic Acid.** P. W. NEBER and E. RÖCKER (*Ber.*, 1923, 56, [B], 1710—1716).—In a recent communication (A., 1922, i, 545), the condensation of *o*-nitrobenzaldehyde with *o*-aminophenylacetic acid

to form *o'*-nitrobenzylidene-*o*-aminophenylacetic acid has been described. The new acid passes by loss of water into a compound which has been formulated provisionally as a quinoline derivative. The unexpected properties of the latter substance have necessitated a revision of the reaction (effected with the more readily obtained benzylidene compound). The products are shown to be derivatives, not of quinoline, but of oxindole. The initial formation of *o'*-nitrobenzylidene-*o*-aminophenylacetic acid is confirmed. The acid when melted or heated in glacial acetic acid solution or in alcohol loses *o*-nitrobenzaldehyde and forms oxindole; the latter substance reacts with the liberated aldehyde to give 3-*o*-nitrobenzylidene-oxindole,  $C_8H_4 \left\langle \begin{array}{c} C(CH_2C_6H_4NO_2) \\ NH \end{array} \right\rangle CO$ .

Benzylideneoxindole, sulphur-yellow needles, m. p.  $176^\circ$ , is obtained directly when benzaldehyde and *o*-aminophenylacetic acid are heated at  $120$ – $130^\circ$  without solvent, in boiling glacial acetic acid or in alcohol containing a little piperidine. It is converted by cautious treatment with barium hydroxide into  $\alpha$ -*o*-aminophenylcinnamic acid,  $CHPh \cdot C(C_6H_4 \cdot NH_2) \cdot CO_2H$ , m. p.  $131^\circ$ , the constitution of which is established by its production from  $\alpha$ -*o*-nitrophenylcinnamic acid (cf. Borsche, A., 1910, i, 35).  $\alpha$ -*o*-2-Naphtholazophenylcinnamic acid,  $C_{25}H_{18}O_3N_2$ , coarse, dark red crystals, incipient decomp.  $215^\circ$ , is described.  $\alpha$ -*o*-Aminophenylcinnamic acid condenses with *o*-nitrobenzaldehyde to give  $\alpha$ -*o'*-nitrobenzylidene-*o*-aminophenylcinnamic acid, pale yellow needles, m. p.  $157^\circ$  after softening at  $154^\circ$ .

Mixtures of molecular quantities of *o*-aminophenylacetic acid and *m*-nitrobenzaldehyde, when heated at  $150^\circ$  or in boiling alcoholic solution in the presence of piperidine, give two products, golden-yellow leaflets, m. p.  $227^\circ$ , and slender, sulphur-yellow needles, m. p.  $204^\circ$ , whereas, according to Bagard and Wahl (A., 1909, i, 330, 735), *m*-nitrobenzylideneoxindole has m. p.  $255$ – $257^\circ$ . 3-*p*-Nitrobenzylideneoxindole forms coarse, red crystals, m. p.  $229^\circ$  after softening at  $227^\circ$ . *o'*-Acetylaminobenzylidene-*o*-aminophenylacetic acid, colourless crystals, m. p.  $143^\circ$ , is converted at  $145$ – $150^\circ$  or in boiling glacial acetic acid solution into 3-*o*-acetylaminobenzylideneoxindole, small, pale yellow needles, m. p.  $221^\circ$ . *o'*-Chlorobenzylidene-*o*-aminophenylacetic acid, colourless needles, m. p.  $127^\circ$ , 3-*o*-chlorobenzylideneoxindole, lemon-yellow needles, m. p.  $178^\circ$ , 3-*m*-chlorobenzylideneoxindole, yellow needles, m. p.  $166^\circ$ , *p'*-chlorobenzylidene-*o*-aminophenylacetic acid, colourless crystals, m. p.  $122^\circ$ , and 3-*p*-chlorobenzylideneoxindole, sulphur-yellow needles, m. p.  $184^\circ$ , are also described. H. W.

**Preparation of Derivatives of 2-Methylquinoline.** KNOLL & Co. (D.R.-PP. 363582 and 363583; from *Chem. Zentr.*, 1923, ii, 915).—Ketone anils are heated with or without the addition of condensing reagents or primary aromatic amines are heated with ketones in the presence of catalysts such as the hydrochlorides of the corresponding primary aromatic amines, zinc chloride, or iodine. The ketone anils used, or formed by the latter

reaction, decompose with evolution of a hydrocarbon and formation of 2:4-dialkylquinolines. By heating acetone anil, or acetone, aniline, and aniline hydrochloride in the presence of condensing reagents, 2:4-dimethylquinoline is obtained, with evolution of methane; it has b. p. 143°/15 mm. Similarly, from methyl ethyl ketoneanil 2-methyl-4-ethylquinoline, b. p. 150—153°/14 mm., is obtained with evolution of ethane. From the condensation product of acetone and *p*-toluidine, 2:4:6-trimethylquinoline, b. p. 146—148°/13.5 mm., m. p. 65.5°, is obtained. Acetophenoneanil gives 4-phenyl-2-methylquinoline with formation of aniline and benzene; it has m. p. 104°.

G. W. R.

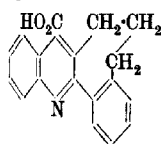
**Benzopolymethylene Compounds. IX. Further Cyclic Analogues of Atophan.** JULIUS VON BRAUN and AUGUST STUCKENSCHMIDT (*Ber.*, 1923, 56, [B], 1724—1729).—Whereas tetrophan, obtained from isatin and 1-keto-1:2:3:4-tetrahydronaphthalene and its dihydro-derivative resemble strychnine in physiological action, the corresponding compound from  $\alpha$ -hydrindone is inactive. It appears, therefore, that the naphthacridine nucleus is the physiologically active component. To test this point, benzosuberone has been converted into the ring-homologue of tetrophan. Unexpectedly, homotetrophan is found to resemble its lower homologue both quantitatively and qualitatively in physiological action. Its constitution has therefore been examined at considerable length, whereby its supposed structure is confirmed. It is possible, therefore, to lengthen the ethylene chain in tetrophan without appreciably changing its pharmacological action.

Benzosuberone, prepared according to the method of Kipping, Hall, and Hunter (*T.*, 1901, 79, 602), is reduced by Clemmensen's method to benzosuberane,  $C_6H_4<\begin{smallmatrix} CH_2 & CH_2 \\ CH_2 & CH_2 \end{smallmatrix}>CH_2$ ,  $d_4^{20}$  0.9693,  $n_D^{20}$  1.5458. The latter substance cannot be dehydrogenated

smoothly by sulphur and only with difficulty by lead oxide-pumice at 700°; naphthalene is thereby obtained, but the presence of methyl-naphthalenes could not be detected. *Homotetrophan* (annexed formula), almost colourless needles, m. p. 294°, is prepared by the action of benzosuberone on isatin in alkaline solution;

the sodium salt is described.

$\gamma$ -Phenyl-*n*-butyl bromide is converted by potassium cyanide into  $\gamma$ -phenyl-*n*-valeronitrile, a colourless liquid, b. p. 125—126°/13 mm., which is hydrolysed by hydrochloric acid at 120° into  $\gamma$ -phenyl-*n*-valeric acid,  $CHMePh\cdot CH_2\cdot CH_2\cdot CO_2H$ , a colourless, viscous liquid, b. p. 165°/12 mm.  $\gamma$ -Phenyl-*n*-valeryl chloride, b. p. 118—119°/13 mm., is converted by aluminium chloride in the presence of carbon disulphide into 1-keto-4-methyl-1:2:3:4-tetrahydronaphthalene,  $C_6H_4<\begin{smallmatrix} CHMe & CH_2 \\ CO & CH_2 \end{smallmatrix}>$ , b. p. 133—134°/13 mm. (*semi-carbazone*, m. p. 204°), which condenses with isatin in the usual



manner to form 4-methyltetrophan (annexed formula), pale yellow needles, m. p. 262°. The latter substance is more active pharmacologically than tetraphan. It is converted, when heated above its melting point, into 4-methyldihydronaphthacridine, a viscous liquid (picrate, m. p. 178°).  $\beta$ -Benzylpropyl bromide is converted successively into  $\beta$ -benzylbutyronitrile, b. p. 121°/13 mm., and  $\beta$ -benzylbutyric acid,  $\text{CH}_3\text{Ph}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , a colourless, viscous liquid, b. p. 161°/13 mm.  $\beta$ -Benzylbutyryl chloride, b. p. 123°/12 mm., is transformed into 1-keio-3-methyl-1:2:3:4-tetrahydronaphthalene, b. p. 127—128°/13 mm.,  $d_4^{20}$  1.0747,  $n_D^{20}$  1.5590 (semicarbazone, m. p. 177°), which condenses with isatin to form 3-methyltetrophan, m. p. 242—243°; the latter substance is physiologically more active than tetrophan. H. W.

**The Constitution of the Dichlorohydroxyethylidenbis-nitroanilines.** ALVIN S. WHEELER and SAMUEL C. SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 1839—1842).—The action of hot dichloroacetic acid and phosphorus pentoxide on *p*-nitroaniline, *o*-nitroaniline, or *m*-nitroaniline gives, respectively, *p*-nitrodichloroacetanilide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CHCl}_2$ , pale yellow needles, m. p. 127°; *o*-nitrodichloroacetanilide, bright yellow plates, m. p. 70—72°, and *m*-nitrodichloroacetanilide, almost colourless needles, m. p. 103°. The *para*-compound appears, together with *p*-nitroaniline, as a decomposition product of the action of hot dilute sulphuric acid on the substance previously described (Wheeler and Glenn, *J. Elisha Mitchell Sci. Soc.*, 1903, 19, 63), as having the constitution  $\text{OH}\cdot\text{CCl}_2\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ ; the compounds having methoxyl (*loc. cit.*) and ethoxyl groups (Wheeler and Smith, *A.*, 1920, i, 93), in place of hydroxyl, give the same products. This reaction determines the position of the hydroxyl (alkoxyl) group in these compounds, which are now to be represented by the formula  $\text{CCl}_2\text{H}\cdot\text{C}(\text{OR})(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ . An exactly similar constitution is ascribed to the *ortho*-compounds (*loc. cit.*), which give *o*-nitroaniline and *o*-nitrodichloroacetanilide on treatment with hot dilute sulphuric acid. W. S. N.

**The Isomerism of the Dinitrobenzidines.** OSCAR LISLE BRADY and GERALD PATRICK MCHUGH (*T.* 1923, 123, 2047—2053).

**Preparation of Derivatives of *para*-Substituted Phenylcarbamides.** C. F. BOEHRINGER & SOEHNE (D.R.P. 367611; from *Chem. Zentr.*, 1923, ii, 909—910).—Derivatives of *para*-substituted phenylcarbamides of the general formula



(where  $\text{R}^2=\text{Me}$  or  $\text{Et}$  and  $\text{R}^1=\text{Me}$ ,  $\text{OME}$ , or  $\text{OEt}$ ) are obtained by introducing the carbamino-group into bases of the formula  $\text{R}^2\cdot\text{C}_6\text{H}_4\cdot\text{NHR}^1$  by known methods. *N*-Methyl-*p*-phenetidine and potassium cyanate in hydrochloric acid solution yield  $\alpha$ -*N*-methyl-*p*-phenetylcarbamide; it forms prismatic crystals, m. p. 137°.

$\alpha$ -N-Methyl-p-anisylcarbamide, from N-methyl-p-anisidine, forms crystals, m. p. 154°.  $\alpha$ -N-Methyl-p-tolylcarbamide is prepared from N-methyl-p-toluidine and carbamide nitrate, and forms small needles, m. p. 102–103°.  $\alpha$ -p-Tolyl-n-ethylcarbamide has m. p. 65°. The introduction of an alkyl group such as methyl or ethyl into the imido-group of a monoarylcarbamide increases both sweetness and solubility in water.

G. W. R.

**The Ternary System Antipyrine-Caffeine-Water. Migranine.** ROBERT KREMANN and EMMERICH JANETZKY (*Monatsh.*, 1923, 44, 49–63).—The authors have studied, in the usual manner, the above ternary system. Antipyrine and caffeine form only a simple eutectic (103°, 13% of antipyrine). Antipyrine and water merely give a eutectic at –3.3° (37.5% of antipyrine). Water and caffeine monohydrate form a eutectic at –0.4°, 4% of caffeine, the transition temperature of caffeine monohydrate-caffeine probably being about 61°, since the solubility curve is broken at this temperature (31% of caffeine). From the ternary diagram constructed, the behaviour, on evaporation, of a mixture of antipyrine (85%), caffeine (8%), and water (7%) (that is, one having approximately the composition of migranine, with added water) is discussed. At 78°, such a mixture would deposit antipyrine. By isothermal evaporation at water-bath temperatures, antipyrine separation would continue, until the solution acquired the composition, antipyrine 81.5, caffeine 13, and water 5.5%. After this, as water was lost, the eutectic mixture of antipyrine and caffeine would separate.

Migranine consists, chemically, of a mixture of caffeine (8.2%) and antipyrine (89.4%), together with small quantities of citric acid (0.56%), combined with the antipyrine. Physically, it consists of the crystalline caffeine-antipyrine eutectic, in which are embedded crystals of antipyrine and of the ternary caffeine-antipyrine-antipyrine citrate eutectic (cf. A., 1920, i, 570).

E. E. T.

**Preparation of Halogen-substituted Barbituric Acid Derivatives.** HERMANN STAUDINGER (Swiss Pats. 93435 and 93749; from *Chem. Zentr.*, 1923, ii, 748).—Diallylbarbituric acid or ethylallylbarbituric acid is treated with hydrobromic acid, preferably in the presence of diluents. The hydrogen bromide is added directly to the double linking in the side-chain with formation of the corresponding bromopropyl derivatives. For example, by the action of 25% hydrobromic acid in acetic acid on diallylbarbituric acid under pressure at 90–100°, di- $\beta$ -bromopropylbarbituric acid is obtained. It is a microcrystalline, white powder with m. p. 237–239°. Ethyl- $\beta$ -bromopropylbarbituric acid forms crystals, m. p. 171–173°.

G. W. R.

**Some Diallylbarbituric Acids with Tertiary Amino-grouping.** ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1923, 45, 1757–1762).—A number of ethyl dialkylmalonates have been prepared in which one alkyl group is ethyl or isoamyl and the other  $\alpha$ -propyl with substitution of a tertiary amino-group

on the  $\gamma$ -carbon atom. From these esters the corresponding barbituric acids have been prepared. The latter, when tested by oral administration to dogs, or by intraperitoneal injection of the alkali solution into white mice, failed to show the hypnotic effect characteristic of the simpler barbituric acids. This inactivity is attributed in some cases to insolubility, in others to a reversal of the distribution coefficient between the two solvents, water and fat (or lipoids).

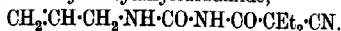
*Ethyl ethyl- $\gamma$ -bromopropylmalonate* is prepared by the action of trimethylene bromide in hot benzene solution on the sodio-derivative of ethyl ethylmalonate, and has b. p.  $169-174^{\circ}/20$  mm. It reacts with diethylamine to give *ethyl ethyl- $\gamma$ -diethylaminopropylmalonate*, a yellow oil, b. p.  $143-149^{\circ}/6$  mm., which is converted by heating at  $108^{\circ}$  with sodium ethoxide and carbamide into *5-ethyl-5- $\gamma$ -diethylaminopropylbarbituric acid*, m. p.  $165-166^{\circ}$ . The following compounds are prepared in an analogous manner. *Ethyl ethyl- $\gamma$ -acetanilidopropylmalonate*, a viscous, yellow oil, b. p.  $244-250^{\circ}/17$  mm. *5-Ethyl-5- $\gamma$ -acetanilidopropylbarbituric acid*, m. p.  $180^{\circ}$ . *Ethyl ethyl- $\gamma$ -acetophenetidinopropylmalonate*, b. p.  $237-240^{\circ}/4$  mm. *5-Ethyl-5- $\gamma$ -acetophenetidinopropylbarbituric acid*, m. p.  $158-159^{\circ}$ . *Ethyl isoamyl- $\gamma$ -bromopropylmalonate*, a viscous oil, b. p.  $175-182^{\circ}/13$  mm. *Ethyl  $\gamma$ -diethylaminopropylisoamylmalonate*, b. p.  $155-161^{\circ}/5$  mm. *5- $\gamma$ -Diethylaminopropyl-5-isoamylbarbituric acid*, m. p.  $133^{\circ}$ . *Ethyl  $\gamma$ -ethylaminopropylisoamylmalonate*, a yellow oil, b. p.  $194-201^{\circ}/4$  mm. *5- $\gamma$ -Ethylaminopropyl-5-isoamylbarbituric acid*, needles, m. p.  $135^{\circ}$ . *Ethyl  $\gamma$ -acetophenetidinopropylisoamylmalonate*, a viscous, yellow oil, b. p.  $245-250^{\circ}/4$  mm. *5- $\gamma$ -Acetophenetidinopropyl-5-isoamylbarbituric acid*, m. p.  $155^{\circ}$ . W. S. N.

**The Course of the Bromination of Allyl-substituted Imino-barbituric Acids.** OTTO DIELS [with KURT WERNER, HUGO BERNHARDT, and RUDOLF RÖHRICHT] (*Annalen*, 1923, **432**, 115-136).—The condensation of allylcarbamide with ethyl diethylcyanoacetate by heating with sodium ethoxide at  $102-105^{\circ}$  leads to the formation of 4-imino-5:5-diethyl-3-allylbarbituric acid (I), m. p.  $109^{\circ}$ , to which the formula  $\text{NH} \begin{smallmatrix} \text{CO} \\ \text{CO-N(C}_2\text{H}_5\text{)} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{—CET}_2 \\ \text{—C:NH} \end{smallmatrix}$  is assigned, in

preference to the alternative structure,  $\text{NH} \begin{smallmatrix} \text{C(NH)CET}_2 \\ \text{CO-N(C}_2\text{H}_5\text{)} \end{smallmatrix} \text{CO}$ .

It is converted by the action of bromine in cold glacial acetic acid solution into the *hydrobromide*, decomp.  $250^{\circ}$ , of 4-bromoimino-5:5-diethyl-3-allylbarbituric acid, glistening tablets, m. p.  $184^{\circ}$ . This compound does not contain the original  $\text{>C:NH}$  group, because it is not hydrolysed by means of dilute mineral acids. Moreover, the allyl radicle is intact, since the compound gives *N-allylveronal*, long needles, m. p.  $79-80^{\circ}$ , on treatment with zinc dust in aqueous alcoholic solution. When reduced in ethereal solution by the aid of aluminium amalgam, the monobromide gives two products: the primary amine,  $\text{NH} \begin{smallmatrix} \text{CO} \\ \text{CO-N(C}_2\text{H}_5\text{)} \end{smallmatrix} \text{CH}_2\text{NH}_2$ ,  $+ \frac{1}{2}\text{H}_2\text{O}$ , m. p.  $131^{\circ}$ , and the corresponding secondary alcohol,

+4H<sub>2</sub>O, m. p. 174°. The latter is also formed from the amine by the action of nitrous acid or of hot acetic acid, and gives, on oxidation by means of chromic acid in warm glacial acetic acid solution, *N*-allylveronal, together with a very small quantity of a compound, m. p. 185°. The amine forms an *ozalate*, and an additive compound, C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>N<sub>3</sub>, PhNCO.H<sub>2</sub>O, m. p. 220°, when ground with phenylcarbimide. When the monoimino-compound is brominated there is formed, in addition to the bromoimino-derivative, a dibromide, C<sub>11</sub>H<sub>17</sub>O<sub>2</sub>N<sub>3</sub>Br<sub>2</sub>, m. p. 120°, which is regarded as *s*-cyanodiethylacetyl-βγ-dibromopropylcarbamide, CH<sub>2</sub>Br·CHBr·CH<sub>2</sub>·NH·CO·NH<sub>2</sub>·CO·CET<sub>2</sub>·CN, for the following reasons. It does not suffer hydrolytic fission when treated with dilute acids, nor does it give *N*-allylveronal when reduced in boiling alcoholic solution by means of zinc dust. Actually the latter reaction gives a compound, C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>N<sub>3</sub>, m. p. 120°, which is stable to hot dilute acids, and is therefore held to be *s*-cyanodiethylacetyl-*n*-propylcarbamide. The dibromide, m. p. 120°, is therefore a derivative, not of the iminobarbituric acid (I), but of the isomeric *s*-cyanodiethylacetylallylcarbamide,



The action of cold glacial acetic acid on the crude product from the condensation of allylcarbamide with ethyl cyanodiethylacetate gives the *acetate*, +2H<sub>2</sub>O, glistening tablets, decomp. 245°, of a *base*, m. p. 90°, which is isomeric with iminodiethylallylbarbituric acid, into which it passes in the course of a few hours. The bromination of the acetate in glacial acetic acid solution does not, however, give the same product as when the imino-compound is used, but the *hydrobromide*, m. p. about 265° (decomp.), of a *monobromide*, thick needles, m. p. 151–152°, to which the con-

stitution  $\begin{array}{c} \text{CO}\cdot\text{CBr}_2\cdot\text{C}\equiv\text{N} \\ \text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{Br}$  is assigned. The production of this compound is assumed to proceed through the dibromide,  $\begin{array}{c} \text{CO}\cdot\text{CET}_2\cdot\text{C}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2 \end{array} \cdot \text{CHBr}\cdot\text{CH}_2\cdot\text{Br}$  in the formation of which the allyl group is reactive. When it is reduced in aqueous alcoholic solution by means of zinc dust, the product is a *base*, C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>N<sub>3</sub>, short, hard crystals, m. p. 246°, which is different from either of the preceding bases of this composition, and is represented by the formula  $\begin{array}{c} \text{CO}\cdot\text{CET}_2\cdot\text{CH}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2 \end{array} > \text{CHMe}$ . It is suggested that the isomerism of the compound (I) and the base, m. p. 90°, may depend on the spatial relationship between the allyl and imino-radicles.

A further example of the formation, in this series, of a dicyclic system is provided by the action of concentrated hydrobromic acid on the compound (I). In the cold, a *hydrobromide*, m. p. 205°, is formed, from which alkali liberates the original material, but if the reaction is conducted at 100°, the product is the *hydrobromide*, m. p. 285°, of an isomeric *base*, C<sub>11</sub>H<sub>17</sub>O<sub>2</sub>N<sub>3</sub>, m. p. 165°, which is formed by the addition of hydrogen bromide to the allyl group, and its subsequent elimination between this and the imino-

radicle. The structure of the bromine-free product will be  $\text{CO}\cdot\text{CEt}_2\cdot\text{C}\equiv\text{N}\cdot\text{CHMe}$  or  $\text{CO}\cdot\text{CEt}_2\cdot\text{C}\equiv\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$ , according as  $\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2$  or  $\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2$  bromine becomes initially attached to the  $\beta$ - or the  $\gamma$ -carbon atom of the allyl radicle, but a choice has not yet been made between these formulæ.

4 : 6-Diimino-5 : 5-diethyl-3-allylbarbituric acid, m. p.  $257^\circ$ , hydrobromide, decomp. above  $255^\circ$ , is prepared by heating allylcarbamide and diethylmalononitrile with ethyl-alcoholic sodium ethoxide at  $102$ – $105^\circ$ ; it is gradually hydrolysed to *N*-allylveronal by means of cold dilute sulphuric acid. The action of bromine on a dilute aqueous suspension of the di-imino-derivative gives the hydrobromide, decomp. above  $210^\circ$ , of a monobromide,  $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}_4\text{Br}$ , in which, by analogy with the monoimino-compound, the bromine is probably attached to that imino-nitrogen atom which is nearer to the allyl group. In agreement with this view, the action of cold concentrated aqueous ammonia on the hydrobromide gives the original di-iminobarbituric acid.

The results clearly demonstrate a striking indifference, towards bromine, of the allyl radicle when in combination with the barbituric acid molecule, by reason of which the attempted preparation of the  $\beta$ -dibromopropyl derivatives has failed.

Moreover, an effort to prepare such compounds, by condensing dibromopropylcarbamide with diethylmalononitrile or ethyl cyanodihethylacetate in the presence of alcoholic sodium ethoxide at  $102$ – $105^\circ$ , has also been unsuccessful, because the sodium ethoxide causes elimination of hydrogen bromide from the dibromopropylcarbamide, with formation of a microcrystalline compound,  $\text{C}_4\text{H}_7\text{ON}_2\text{Br}$ , m. p.  $146^\circ$ , apparently the sole product of the reaction. W. S. N.

5 : 5-Diarylbarbituric Acids. ARTHUR W. DOX and ADRIAN THOMAS (*J. Amer. Chem. Soc.*, 1923, **45**, 1811–1816).—Ethyl diphenylmalonate, white prisms, m. p.  $58$ – $59^\circ$ , b. p.  $180$ – $200^\circ/9$  mm., is prepared by the interaction of benzene and ethyl mesoxalate in the presence of warm concentrated sulphuric acid. When it is heated with alcoholic sodium ethoxide and carbamide at  $106$ – $108^\circ$ , diphenylbarbituric acid is not produced, but loss of carbon dioxide occurs, with formation of diphenylacetic acid, diphenylacetamide, and traces of diphenylmethane. Ethyl di-*p*-tolylmalonate behaves similarly, giving di-*p*-tolylacetic acid, and di-*p*-tolylacetamide, white needles, m. p.  $190^\circ$ . Phenol and ethyl mesoxalate react in the cold in the presence of dry hydrogen chloride, giving ethyl di-*p*-hydroxyphenylmalonate, flat, lustrous needles, m. p.  $133$ – $134^\circ$ , which gives a blue coloration with ferric chloride, and readily condenses when heated with carbamide and sodium ethoxide, with formation of 5 : 5-di-*p*-hydroxyphenylbarbituric acid, small, slender needles, m. p.  $288$ – $290^\circ$ . Ethyl di-6-hydroxy-*m*-tolylmalonate, short, white prisms, m. p.  $107$ – $108^\circ$  and 5 : 5-di-6'-hydroxy-*m*-tolylbarbituric acid, white prisms, m. p.  $217$ – $219^\circ$ , are prepared similarly from *o*-cresol. 5 : 5-Diphenylbar-

barbituric acid, slender, white needles, m. p. 192°, is prepared from ethyl diphenoxymalonate, b. p. 195–204°/6 mm., which is prepared from sodium phenoxide and ethyl dibromomalonate in boiling alcoholic solution.

Since intraperitoneal injection of di-*p*-hydroxyphenylbarbituric acid or diphenoxybarbituric acid into white mice does not produce coma or even muscular inco-ordination, even when the dose is twice as large as that which produces profound coma within fifteen minutes when veronal is used, it is concluded that these substances are physiologically inert.

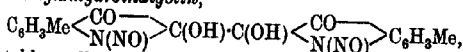
W. S. N.

**2-Ethylaminoindole Hydrochloride from Rutaecarpine.** YASUHIKO ASAHINA and the DAICHI SEIYAKU KABUSHIKI KAISHA (Japan Pat. 41593).—Five g. of rutaecarpine are boiled with 40 c.c. of amyl alcohol and 40 g. of powdered potassium hydroxide; after cooling, it is mixed with 50 c.c. of water, and the alcohol is separated. After filtration, the larger part of the solvent is distilled off and the liquid nearly neutralised with dilute phosphoric acid; white, silky crystals (about 3.1 g.) of 2-ethylaminoindole-carboxylic acid are deposited. By boiling these with 5% hydrochloric acid for two to three hours, the acid is decomposed into carbon dioxide and the amine, which is extracted with ether. Colourless scales of 2-ethylaminoindole hydrochloride, m. p. 245–246°, are obtained by passing hydrogen chloride into the ethereal solution.

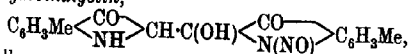
K. K.

**The Indigo Group. III. The Action of Nitrous Fumes on 7:7'-Dimethylindigotin.** THEODOR POSNER and WALTER HEUMANN (*Ber.*, 1923, 56, [B], 1621–1629).—The action of nitrous fumes on 7:7'-dimethylindigotin is, in general, precisely analogous to the action on indigotin itself; certain secondary changes which appear to differ in the two cases will be described in a subsequent communication.

The primary intermediate product, 1:1'-dinitroso-2:2'-dihydroxy-7:7'-dimethyldihydroindigotin,



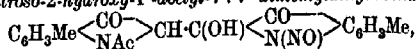
an unstable, yellowish-brown powder, is obtained by the action of nitrous fumes on a suspension of 7:7'-dimethylindigotin in ether. It is converted by alcohol into 1-nitroso-2-hydroxy-7:7'-dimethyldihydroindigotin,



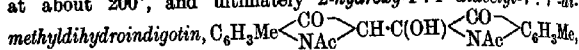
pale yellow, crystalline powder, m. p. 198–200° (decomp.), after darkening at about 185°. The yield of this substance is only 20–25% of the initial material, which is also decomposed to ethyl *m*-toluoylformate (see later) and 7-methylisatin, tile-red needles, m. p. 266° (*phenylhydrazone*, golden yellow needles, m. p. 12°). Nitrosohydroxydimethyldihydroindigotin is converted by aqueous ammonia into a compound,  $\text{C}_{18}\text{H}_{13}\text{O}_3\text{N}_3$ , pale, golden-brown needles, m. p. 265–266°, the constitution of which has

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not been definitely elucidated; this reaction differs from that observed with the corresponding derivative of indigotin. Nitroso-hydroxydimethyldihydroindigotin can be cautiously recrystallised from glacial acetic acid. Protracted treatment with the acid gives 1-nitroso-2-hydroxy-1'-acetyl-7:7'-dimethyldihydroindigotin,



golden-yellow crystals, m. p. 237—239° (decomp.) after darkening at about 200°, and ultimately 2-hydroxy-1:1'-diacetyl-7:7'-di-



a yellow, crystalline powder which darkens above 250°, but does not melt below 300°.

The action of nitrous fumes on 7:7'-dimethylindigotin suspended in glacial acetic acid proceeds similarly to that on indigotin. In this case, however, the intermediately-formed dinitrosodiacetyryl-7:7'-dimethyldihydroindigotin is too unstable to permit its isolation and nitrosohydroxy-7:7'-dimethyldihydroindigotin is obtained. If adequate cooling is not provided, 7-methylisatin is formed.

When nitrous fumes are passed into a suspension of 7:7'-dimethylindigotin in methyl or ethyl alcohol, 7-methylisatin is formed and ultimately converted into the ester of *m*-toluoylformic acid. *Methyl m-toluoylformate*,  $\text{C}_6\text{H}_5\text{Me} \cdot \text{CO} \cdot \text{CO}_2\text{Me}$ , has b. p. 137—138°/11—12 mm., 245—250° (slight decomp.)/763 mm. *Ethyl m-toluoylformate* has b. p. 140—142°/11—12 mm., 250—255° (partial decomp.)/atmospheric pressure. Hydrolysis of the esters gives *m-toluoylformic acid*, m. p. 80—82° (*phenylhydrazine*, m. p. 158°). H. W.

**2-Pyridylpyrroles.** A. E. TSCHITSCHIBABIN and J. E. BYLINKIN (*Ber.*, 1923, 56, [B], 1745—1749).—Attempts are described to prepare pyridylpyrroles from 2-aminopyridine on the lines developed by Pictet for the synthesis of nicotine from 3-amino-pyridine.

N-2-Pyridylpyrrole,  $\begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{array} \text{N} \cdot \text{C}_5\text{H}_4\text{N}$ , is obtained by distill-

ation of a mixture of 2-aminopyridine, mucic acid, and aluminium oxide; it is conveniently separated from unchanged 2-aminopyridine by means of benzoic anhydride. It is an almost colourless liquid, b. p. 123°/11 mm., 250°/748 mm. It dissolves in cold aqueous sulphuric or hydrochloric acids to colourless solutions which become intensely purplish-red when warmed. The *chloroplatinate*,  $(\text{C}_5\text{H}_4\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , a microcrystalline, yellow powder which slowly decomposes without melting when heated and the *picrate*, needles, m. p. 141°, are described. The base is isomerised when passed through a heated tube to 2-pyridyl

2'-pyrrole,  $\begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{NH} \end{array} \text{CH} \cdot \text{C}_5\text{H}_4\text{N}$ , small, colourless prisms, m. p.

87—88° [*chloroplatinate*,  $(\text{C}_5\text{H}_4\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , small needles *picrate*, yellow needles or prisms, m. p. 221°]. The latter substance is converted by the successive action of metallic potassium and

methyl toluene-*p*-sulphonate into *N*-methyl-2-pyridyl-2'-pyrrole [a-nicotyrin],  $\begin{array}{c} \text{OH}-\text{CH} \\ \text{CH}-\text{NM}_6 \end{array} \text{C}_6\text{H}_4\text{N}$ , an almost colourless liquid which becomes dark red when preserved, b. p. 149–150°/22 mm. [*chloro-platinate*,  $(\text{C}_{10}\text{H}_{10}\text{N}_2)_2\text{H}_2\text{PtCl}_6$ , dark, orange-coloured needles; *picrate*, small, yellow leaflets, m. p. 138–139°]. H. W.

**Synthesis of Diphenylguanidine.** J. D. BRUMBAUGH (*Chem. Age (N.Y.)*, 1923, **31**, 175–176).—Ethyl alcohol (*d* 0.87) at 75° is saturated with ammonia, and a mixture of diphenylthiocarbamide and zinc oxide is added. Ammonia is passed through the stirred mixture at 75° for three hours, or until desulphurisation is complete. The hot solution is filtered and poured into dilute ammonia solution, which precipitates diphenylguanidine,  $\text{NH}_2\text{C}(\text{NHPh})_2$ , n 67% yield.

## CHEMICAL ABSTRACTS.

**Reduction of Uric Acid Glycols—A Contribution to the Characterisation of their Hydroxyls.** HEINRICH BILTZ and RUDOLF LEMBERG (*Annalen*, 1923, **432**, 137–176).—This research is primarily concerned with the influence of the hydroxyl group in the position 4, in promoting the fission of the bond 3:4 in derivatives of uric acid.

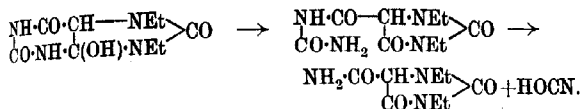
The reduction of uric acid glycols to uric acids by means of hydriodic acid was previously unsuccessful, apparently because the presence of the hydroxyl group in position 4 facilitates the disruption of the bond 3:4 (Biltz and Heyn, A., 1912, i, 589). His behaviour is unaffected by etherification of the 5-hydroxyl group, but the diethers are readily reduced to the uric acids. Since 7:9-dimethyl- and 4:5-dichloro-7:9-dimethyl-4:5-dihydrouric acids are readily reduced to the respective uric acids by means of strongly acid stannous chloride, an attempt has now been made to replace the hydroxyl groups of the glycols by halogen. 4:5-Dihydroxy-7:9-dimethyl-4:5-dihydrouric acid gradually dissolves in phosphorus oxychloride at 100°, with formation of 5-chloro-4-hydroxy-7:9-dimethyl-4:5-dihydrouric acid, together with traces of the 4:5-dichloro-derivative. The presence of the latter is evident from the formation of 7:9-dimethyluric acid by the reduction, by means of zinc dust and glacial acetic acid, of the residue left after distilling off the excess of phosphoryl chloride under reduced pressure; 7:9-diethyluric acid could not, however, be obtained in this way. The formation of the monochloro-compound is demonstrated by treating the phosphoryl chloride solution with ethyl or ethyl alcohol, whereby the 4-hydroxy-5-alkoxy-derivative is produced. 5-Ethoxy- and 4-hydroxy-5-methoxy-7:9-dimethyl-4:5-dihydrouric acids have been prepared in this manner, so 4-hydroxy-5-ethoxy-7:9-diethyl-4:5-dihydrouric acid, large, four-sided, domed prisms, m. p. 179°, and 4-hydroxy-5-methoxy-7:9-dimethyl-4:5-dihydrouric acid, hexagonal tablets, rhombohedra, or *n*-sided, domed prisms, m. p. 130–131°. These results confirm any previous observations which have demonstrated the reactivity

of the hydroxyl group in position 5 of the uric acid and *pseudouric* acid derivatives.

The action of phosphorus tribromide at 100° on 7:9-diethyl- or 4:5-dihydroxy-7:9-dimethyl-4:5-dihydrouic acids, followed by extraction by means of water, ethyl alcohol, or, better, methyl alcohol, gives, respectively, 4-hydroxy-7:9-diethyl-4:5-dihydrouic acid, slender needles, or elongated leaflets, m. p. 199–200° (ammonium salt), and 4-hydroxy-7:9-dimethyl-4:5-dihydrouic acid, rectangular leaflets, or flat prisms, m. p. 200–201° (ammonium salt). The same reaction ensues by the use of phosphorus trichloride or of commercial phosphorus oxybromide containing the trihalide; the use of phosphorus trihalides as reducing agents is discussed, and illustrated by many examples drawn from the literature. The reduction of the 4:5-dihydroxy-derivatives of 9-methyl-, 9-ethyl-, or 3:7-dimethyl-4:5-dihydrouic acids could not be effected, apparently because these substances only react at temperatures higher than the boiling point of phosphorus tribromide. When treated in the same way, 4:5-dihydroxy-4:5-dihydrouic acid is converted into *spirodihydantoin*. The monohydroxy-acids rapidly reduce cold ammoniacal silver nitrate solution (cf. following abstract). The diethyl-acid has a bitter taste, but is physiologically inactive when administered to frogs or dogs (Pohl). The action of chlorine in aqueous solution on the monohydroxy-acids gives the dihydroxy-acids, but in ethyl- or methyl-alcoholic solution, the product is the 4-hydroxy-5-ethoxy- or 4-hydroxy-5-methoxy-acid, respectively. Chlorination of 4-hydroxy-7:9-diethyl-4:5-dihydrouic acid in glacial acetic acid solution gives the monohydrate of 5-hydroxy-1:3-diethylhydantoylamide (see below). The action of hot concentrated hydrochloric acid on 4-hydroxy-7:9-dimethyl-4:5-dihydrouic acid converts it into carbamide and 1:3-dimethylhydantoin.

It is characteristic of the 4-hydroxy-4:5-dihydrouic acids that the hydroxyl group may readily be methylated by the action of diazomethane in cold, moist ethereal solution. In this way, the 7:9-diethyl acid and the 7:9-dimethyl acid give, respectively, 4-methoxy-7:9-diethyl-4:5-dihydrouic acid, glistening, flat prisms, m. p. 200°, and 4-methoxy-7:9-dimethyl-4:5-dihydrouic acid, m. p. 190–195°, *monohydrate*, long, glistening, four-sided prisms, m. p. 190–195° (decomp.), whilst 4-methoxy-3:7-dimethyl-4:5-dihydrouic acid, prisms, m. p. 194°, is similarly obtained from 4-hydroxy-3:7-dimethyldihydrouic acid. The preparation of the latter (Biltz and Damm, A., 1914, i, 1093), from the 5-chloro-4-hydroxy-acid, has been improved, the reduction now being effected by the use of zinc dust and glacial acetic acid. By the action of chlorine in absolute methyl-alcoholic solution, the 4-methoxy-7:9-diethyl- and 4-methoxy-7:9-dimethyl-dihydrouic acids are converted into 4-hydroxy-5-methoxy-7:9-diethyl- and 4-hydroxy-5-methoxy-7:9-dimethyl-4:5-dihydrouic acids, respectively, the introduction of the methoxyl radicle in position 5 being accompanied by the hydrolysis of the existing methoxyl group in position 4. This is partly avoided by working at a temperature below 0°.

It is remarkable that elimination of water from the positions 4 and 5 of the 4-hydroxy-4:5-dihydrouric acids does not occur; this confirms a previous suggestion (Biltz and Damm, *loc. cit.*) that the hydrogen atom in position 5 and the hydroxyl group in position 4 are on opposite sides of the ring. Actually the influence of the 4-hydroxyl radicle promotes an entirely different kind of change. Thus, when 4-hydroxy-7:9-diethyl-4:5-dihydrouric acid is heated at 230–250°, instead of water, cyanic acid (isolated as cyanuric acid) is eliminated, with formation of 1:3-diethylhydantoylamide, hard, four- or six-sided prisms, m. p. 110°; this reaction undoubtedly proceeds through 1:3-diethylhydantoylcarbamide according to the scheme:

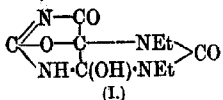


1:3-Diethylhydantoylamide has a bitter taste, and instantaneously reduces cold ammoniacal silver nitrate solution. It is oxidised in aqueous solution by means of chlorine, giving 5-hydroxy-1:3-diethylhydantoylamide, the *monohydrate* of which forms hard, hexagonal tablets, m. p. 90–100°. If the chlorination of diethylhydantoylamide is carried out in ethyl-alcoholic solution, 5-ethoxy-1:3-diethylhydantoylamide is formed. The thermal decomposition of the hydroxy-7:9-dimethyl acid at 230° gives cyanic (cyanuric) acid, and 1:3-dimethylhydantoylamide, leaflets, m. p. 181°, which is oxidised by the action of cold ammoniacal silver nitrate solution, and gives, on treatment with chlorine in aqueous solution, 5-hydroxy-1:3-dimethylhydantoylamide. The previous statement (Biltz, A., 1910, i, 521) that the latter reduces ammoniacal silver nitrate solution was erroneous. A *monohydrate* of this amide, hard, four-sided prisms (? monoclinic), m. p. 180–182°, is described. The thermal disruption of the bond 3:4 is apparently inhibited to some extent by substitution in position 3, since this decomposition is not effected when 4-hydroxy-3:7-dimethyl-4:5-dihydrouric acid is heated at 250°; the only pure product isolated is a compound,  $\text{C}_8\text{H}_8\text{O}_3\text{N}_3$ , prisms, or leaflets, m. p. 210°, isomeric with trimethyl isocyanurate. Fission of the bond 3:4 does, however, occur when 4:5-dihydroxy-3:7-dimethyl-4:5-dihydrouric acid is left in contact with pyridine and methyl alcohol, with formation of  $\alpha$ -5-hydroxy-1-methylhydantoyl- $\beta$ -methylcarbamide. 4:5-Dihydroxy-7:9-diethyl- and 4:5-dihydroxy-7:9-dimethyl-4:5-dihydrouric acids undergo the same reaction, giving, respectively, 5-hydroxy-1:3-diethylhydantoylcarbamide and 5-hydroxy-1:3-dimethylhydantoylcarbamide, m. p. 216° (Biltz, *loc. cit.*). W. S. N.

#### Dioxin Degradation of 4-Hydroxy-4:5-dihydrouric Acids.

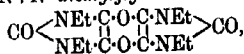
LEINRICH BILTZ and RUDOLF LEMBERG (*Annalen*, 1923, 432, 177–77).—4-Hydroxy-7:9-diethyl-4:5-dihydrouric acid (cf. preceding

abstract) is oxidised by means of warm ammoniacal silver nitrate solution, or warm ferric chloride solution, or, better, by the action of air on its solution in methyl alcohol and pyridine, to 2 : 5-oxido-4-hydroxy-6 : 8-diketo-7 : 9-diethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine (I), leaflets, m. p. 209—210° (decomp.); but oxidation by means of potassium



dichromate gives 4 : 5-dihydroxy-7 : 9-diethyl-4 : 5-dihydrouric acid. That the hydrogen in position 5 is utilised in forming the oxido-compound is demonstrated by its indifference to ammoniacal silver nitrate solution, or aqueous or alcoholic chlorine. The compound (I) is readily methylated by means of moist ethereal diazomethane, giving 2 : 5-oxido-4-methoxy-6 : 8-diketo-7 : 9-diethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine, hexagonal prisms, m. p. 198° (slight decomp.). The same compound is obtained by oxidising 4-methoxy-7 : 9-diethyldihydrouric acid by means of warm ferric chloride solution; hence the compound (I) contains the original 4-hydroxy-group intact. That the second hydrogen atom comes from position 1, and not from position 3, is evident, since hydroxy-3 : 7-dimethyldihydrouric acid undergoes a similar series of changes. If the hydrogen were directly derived from position 1, a three-membered ring would be formed. This is unlikely; hence enolisation must intervene. The subsequent elimination of the two hydrogen atoms can then only lead to a compound having the structure (I). The compound (I) gradually dissolves in boiling water with elimination of carbon dioxide and ammonia, and formation of the lactone of 5-hydroxy-1 : 3-diethylglyoxalone-4-carbamie acid, (II)  $\text{CO} < \begin{array}{c} \text{O}-\text{C} \cdot \text{NEt} \\ | \\ \text{NH}-\text{C} \cdot \text{NEt} \end{array} > \text{CO}$ , rhombohedra, m. p. 146—148°

(decomp.). This compound behaves as a lactone towards aqueous alkali hydroxides (titration). It may be methylated by means of moist ethereal diazomethane, giving the lactone of 5-hydroxy-1 : 3-diethylglyoxalone-4-methylcarbamie acid, four-sided prisms, m. p. 228—229°. Since this acid gives methylamine when boiled with sodium hydroxide solution, the entering methyl group must have become attached to nitrogen. In the production of the compound (II), therefore, the reactive 4-hydroxyl radicle has disappeared from the compound (I), being removed, together with hydrogen from position 5, as water, subsequent to the elimination of nitrogen (position 1) as ammonia and carbonyl (position 6) as carbon dioxide. The alternative removal of nitrogen from position 3 is excluded because (a) this would lead to the known lactimide of 5-hydroxy-1 : 3-diethylhydantoin-5-carboxylic acid, and, (b) in the corresponding degradation of the 3 : 7-dimethyl acid, ammonia, and not methylamine, is removed at this stage. The compound (II) is converted by the action of boiling aqueous alkali carbonate or hydroxide into bis-N : N'-diethylglyoxalonodiazin (III),



long prisms, m. p. 165—166°, which is also formed by the action of

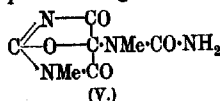
boiling sodium carbonate solution on 2:5-oxido-4-methoxy-6:8-diketo-7:9-diethylhexahydropurine, and is a by-product in the preparation of the lactone (II). This compound is extraordinarily stable; it is not acidic, and does not react with aqueous bromine, with boiling concentrated hydrochloric acid, or with aniline at 215–220°. It is, however, gradually decomposed by the action of boiling 50% aqueous potassium hydroxide, with elimination of ethylamine, but only a small quantity of a substance, m. p. about 80°, perhaps diethylcarbamide, is isolated. Nevertheless, the compound (III) is oxidised by means of chromic acid in boiling aqueous sulphuric acid solution, the product being diethylparabanic acid. The structure (IV), 
$$\text{OC} \begin{array}{c} \text{NEt} \cdot \text{CO} \\ \text{NEt} \cdot \text{C} = \text{C} \cdot \text{CO} \cdot \text{NEt} \end{array} \text{CO}$$
, also ex-

presses this decomposition, but the dioxin formula is preferred by reason of the inertness of the substance towards bromine or boiling concentrated nitric acid. Its production from the lactone (II) by the union of two molecules, subsequently to the removal of the  $-\text{OC} \cdot \text{NH}-$  group as carbon dioxide and ammonia, may more readily be reconciled with the formula adopted.

4-Hydroxy-7:9-dimethyl-4:5-dihydrouric acid suffers the same degradation, excepting that the intermediate lactone corresponding with (II) is not isolated. Oxidation of the 7:9-dimethyl acid may be accomplished with the aid of atmospheric oxygen, using the pyridine-methyl alcohol solution, or, very conveniently, by means of ferric chloride solution, and gives 2:5-oxido-4-hydroxy-6:8-diketo-7:9-dimethyl-3:4:5:6:8:9-hexahydropurine, cf. formula (I), domed prisms, m. p. 230° (decomp.), methyl ether, small rhombohedra, m. p. 230° (decomp.). The oxido-derivative gradually dissolves when boiled with dilute hydrochloric acid, giving a compound, rhombohedra, m. p. 317°, for which, however, no formula has been devised. By the action of boiling water alone, the oxido-compound passes into *bis*-N':N'-dimethylglyoxalonodioxin, domed prisms, m. p. 228°, which gives dimethylparabanic acid on oxidation by means of chromic acid.

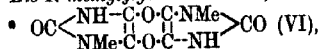
The analogous degradation of 4-hydroxy-3:7-dimethyl-4:5-dihydrouric acid has also been accomplished, but with difficulty. The action of atmospheric oxygen in the presence of pyridine and methyl alcohol, or the use of 10% ferric chloride solution, gives the 4:5-dihydroxy-acid, but the use of 5% ferric chloride solution leads to the formation of 2:5-oxido-4-hydroxy-6:8-diketo-3:7-dimethyl-3:4:5:6:8:9-hexahydropurine,  $+1\frac{1}{2}\text{H}_2\text{O}$ , small rhombohedra, m. p. 186° (decomp.). When the latter is treated with moist ethereal diazomethane, methyl groups enter on both oxygen and nitrogen, giving 2:5-oxido-4-methoxy-6:8-diketo-3:7:9-trimethyl-3:4:5:6:8:9-hexahydropurine, small, four-sided prisms, m. p. 178–179° (decomp.). This compound is also formed by the methylation of 2:5-oxido-4-methoxy-6:8-diketo-3:7:9-trimethylhexahydropurine, prisms, m. p. 205–206° (decomp.), which is obtained by oxidising the 4-methoxy-3:7-dimethyl acid by means of 5% ferric chloride solution. The oxido-3:7-dimethyl compound undergoes isomerisation when boiled for a short time with water, the

product being 2:5-oxido-4:6-diketo-5-( $\alpha$ -methylcarbamido)-3-methyl-



3:4:5:6-tetrahydropyrimidine (V), hard rhombohedra, m. p. 245° (decomp.). The production of this isomeride, by fission of the glyoxalone ring, is obviously dependent on the presence of the hydr-

oxyl group in position 4. The reverse change is effected by dissolving in dilute sodium hydroxide solution, followed by acidification; it is also brought about by the agency of diazomethane, since on methylation the isomeride gives the same methoxytrimethylhexahydropurine derivative as the original oxido-compound. On boiling with water for a longer period, the oxido-compound gradually passes, with generation of carbon dioxide and ammonia, into the lactone of 5-hydroxy-1-methylglyoxalone-4-methylcarbamic acid, cf. formula (II), four-sided prisms, m. p. 263–264° (decomp.), which gives methylparabanic acid on oxidation by means of chromic acid, and therefore still contains the glyoxalone ring. The lactone passes on methylation, using diazomethane, into the lactone of 5-hydroxy-1:3-dimethylglyoxalone-4-methylcarbamic acid, short, four-sided prisms, m. p. 172–173° (slight decomp.). The conversion of the lactone, m. p. 263–264°, into the dioxin derivative proceeds with greater difficulty than in the other two series investigated. Neither boiling water nor boiling 10% sodium hydroxide solution suffices, but the change is brought about by boiling with 20% potassium hydroxide solution or with concentrated hydrochloric acid. Bis-N-methylglyoxalonodioxin,



short, flat, four-sided prisms, m. p. 327° (decomp.), gives methylparabanic acid on oxidation by means of chromic acid. It is acidic, owing to the presence of two  $\text{-NH}\cdot\text{CO-}$  groups. On treatment with moist ethereal diazomethane, two methyl groups enter, with production of bis-N:N'-dimethylglyoxalonodioxin (above). The latter is also formed by the action of boiling 10% sodium carbonate solution on the lactone of 5-hydroxy-1:3-dimethylglyoxalone-4-methylcarbamidic acid. W. S. N.

**Mercaptans of the Purine Group.** I. SIR PRAFULA CHANDRA RÂY, GOPÂL CHANDRA CHAKRAVARTI, and PRAFULA KUMÂR BOSE (T., 1923, 123, 1957–1962).

**The Configuration of Naphthalene Azo-dyes possessing Affinity for Cellulose.** II. N. N. VOROSHOV and K. A. GRIBOV (Bull. Inst. Polytech. Ivanovo-Voznesensk, 1923, 7, 102–109).—It has already been suggested (*ibid.*, 1921, 4, 95) that the substantivity of naphthalene azo-dyes to cotton is dependent on the presence of two or more nitrogenous substituents, one of these being an azo-group, in certain relative positions. A number of azo-compounds possessing a nitro-group in different positions have now been studied and 1:4-, 1:5-, 2:6-, and 2:8-nitroamino-compounds were found to give substantive cotton

dyes on diazotisation and coupling with various substances such as Cleve's acid, N and W acid, H acid, etc. [Cf. *J.S.C.I.*, 1923, 42, 822A].

G. A. R. K.

**The Isosterism of Phenylcarbimide and Diazobenzene-imide.** WALLACE H. CAROTHERS (*J. Amer. Chem. Soc.*, 1923, 45, 1734—1738).—Assuming the atoms of phenylcarbimide and of diazobenzeneimide to be arranged as indicated by the formulæ  $\text{Ph}\cdot\text{N}\cdot\text{C}\cdot\text{O}$  and  $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{N}$ , application of the octet theory leads to the conclusion that they are isosteric. They should therefore be very similar in their physical properties. Measurements of their densities, vapour pressures, and viscosities at various temperatures have confirmed this prediction. The densities (g./c.c.) are expressed by the following equations: for phenylcarbimide,  $d=1\cdot1152-0\cdot001044t$ , and for diazobenzeneimide,  $d=1\cdot1152-0\cdot001044t$ , where  $t=t-2\cdot44^\circ$ . The vapour pressures are given by the equation: for phenylcarbimide,  $p=157-4\cdot76t+0\cdot042t^2$ , and for diazobenzeneimide,  $p=157-4\cdot76t+0\cdot042(t')^2$ , where  $t'=t-1\cdot7^\circ$ . The viscosities (centipoises) are expressed as follows: for phenylcarbimide,  $\eta=1\cdot326-0\cdot02163t+0\cdot000174t^2$ , and for diazobenzeneimide,  $\eta=1\cdot326-0\cdot02163t'+0\cdot000174(t')^2$ , where  $t'=t-4\cdot8^\circ$ .

W. S. N.

**Halogenated Aromatic Hydrazines. I. The True 3:4-Dibromophenylhydrazine, and Meyer's so-called 3:4-Dibromophenylhydrazine.** ÉMILE VOTOČEK and P. JIRŮ (*Bull. Soc. chim.*, 1923, [iv], 33, 918—934).—3:4-Dibromophenylhydrazine, prepared from 3:4-dibromoaniline, crystallises from light petroleum in yellow needles, m. p.  $75^\circ$ , and is not identical with the supposed 3:4-dibromophenylhydrazine, m. p.  $104^\circ$ , described by Meyer (*A.*, 1893, i, 155). Its *hydrochloride* decomposes at  $215^\circ$ , the normal *sulphate* at  $180^\circ$ , and the *acid sulphate* at  $135^\circ$ . The *oxalate* is soluble with difficulty and decomposes at  $162-163^\circ$ , the *picrate* forms yellow needles decomposing at  $154-156^\circ$ . The *acetyl* derivative forms pale red needles, m. p.  $181-182^\circ$ . 3:4-Dibromophenylhydrazine forms *hydrazones* with *benzaldehyde*, m. p.  $128^\circ$ ; *salicylaldehyde*, m. p.  $190^\circ$ ; *acetone*, an oil; *arabinose*, m. p.  $82-83^\circ$ ; *rhamnose*, m. p.  $153-154^\circ$ , and *dextrose*, m. p.  $165-167^\circ$ . It forms an *osazone* with *dextrose* or *lævulose*, m. p.  $225-226^\circ$  (decomp.). This brominated phenylhydrazine is not suitable for the characterisation of sugars because it yields derivatives which are difficult to purify.

Meyer's so-called 3:4-dibromophenylhydrazine is shown to be 4-bromophenylhydrazine, which is obtained by the bromination of acetophenylhydrazone according to the following scheme. One atom of bromine enters the nucleus in the para-position, and the hydrogen bromide so formed combines with the acetone-*p*-bromophenylhydrazone to give the hydrobromide. This decomposes to form *p*-bromophenylhydrazine hydrobromide. Further addition of bromine causes the formation of an *N*-bromo-derivative, which undergoes transformation into 2:4-dibromophenylhydrazine, small quantities of which are formed in the preparation of 4-mono-bromophenylhydrazine by Meyer's method.

H. H.

**Protein Coagulation by Drops. II.** J. BEČKA and F. ŠINKORA (*Biochem. Z.*, 1923, 138, 326—334).—From observations on drops of horse-serum arranged in successive rows on a glass plate (cf. this vol., i, 717), it is concluded that with increasing electrolyte concentration the coagulation by mercuric-ions falls off, whereas that by hydrogen-ions increases. The kations as a rule follow Hofmeister's series, but a reversal is observed in acid solution when the concentration of the kation is above  $M/4$ . The action of carbamide in increasing the precipitating action of mercuric-ions and hydrogen-ions is proportional to its concentration. H. K.

**Protein Coagulation by Drops. III.** J. BEČKA and F. ŠINKORA (*Biochem. Z.*, 1923, 138, 335—340).—The precipitating action on horse-serum of mercuric chloride, copper sulphate, phenol, resorcinol, and catechol was studied by the drop on plate method. Having determined the limits of coagulation, the authors determined the new limits for mixtures of two or more of these coagulants. The precipitating effect of mixtures is greater than that of either component. H. K.

**The Digestibility of Proteins in Vitro. IV. The Digestibility of the Cotton Seed Globulin and the Effects of Gossypol on the Peptic-Tryptic Digestion of Proteins.** D. BREYSE JONES and HENRY C. WATERMAN (*J. Biol. Chem.*, 1923, 56, 501—511).—When treated successively with pepsin and trypsin in vitro, the globulin isolated from cotton seed is digested at practically the same rate as casein. The digestion of both proteins is, however, interfered with if gossypol is added to the mixture in approximately the same proportion as it is present in cotton seed. These results confirm the view of Alsberg and Schwartz (*J. Pharm. Expt. Ther.*, 1921, 17, 344) that the incomplete digestion in vivo of the proteins in cotton seed flours is due to the presence in the latter of gossypol. E. S.

**Influence of Moisture on the Diminution in the Solubility of Casein by the Action of Lactic Acid.** MARC FOUASSIER (*Bull. Soc. Chim. biol.*, 1923, 5, 487—490).—Experiments are described which show that the diminution in solubility which occurs on keeping certain types of dried milk is due to the presence of moisture. In the presence of small amounts of moisture the lactic acid contained in the milk renders the casein insoluble. E. S.

**Metallic Compounds of Proteins.** A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1923, 42, 620—622).—The author has precipitated the proteins of milk with equivalent quantities of copper sulphate, chloride, nitrate, and acetate, and has analysed both the precipitate and the filtrate. It is found that the amount of copper in the precipitate increases with the amount of copper added. In the case of the sulphate, it is shown that a variable amount of the anion is precipitated, so that it is impossible to state that an equilibrium is set up between the protein and the copper sulphate, as has previously been done by Galeotti (*A.*, 1904, i, 355). J. F. S.

**Electrical Conductivity of Caseinates.** FRIEDRICH PLATTNER (*Kolloid Z.*, 1923, 33, 98—101).—The electrical conductivity of alkali caseinate solutions has been measured at 25° at various periods after preparation. It is shown that caseinate solutions preserved under toluene do not change. A 1.2% solution had a conductivity  $6.78 \times 10^{-4}$  ohms<sup>-1</sup> and eleven days later the solution had a conductivity  $6.80 \times 10^{-4}$ . More concentrated solutions showed a similar stability. J. F. S.

**Reaction between Proteins and Nitrous Acid. The Tyrosine Content of Deaminised Casein.** HOWARD B. LEWIS and HELEN UPDEGRAFF (*J. Biol. Chem.*, 1923, 56, 405—414).—In the deamination of casein by nitrous acid the destruction of amino-acids other than lysine is probably due to secondary reactions. In the present paper, it is shown that the maximum amount of tyrosine is present in deaminised casein when deamination is carried out at low temperatures. If such deaminised casein is treated with acetic acid and sodium nitrite, the tyrosine content is diminished, the diminution being proportional to the time of action and the temperature. E. S.

**A New Sulphur-containing Amino-acid isolated from Casein.** J. H. MUELLER (*Proc. Soc. Expt. Biol. Med.*, 1921, 19, 161—163).—Commercial casein (13,608 g.) was hydrolysed with sulphuric acid, neutralised with sodium carbonate, and precipitated with mercuric sulphate solution; from the washed precipitate freed from electrolytes a second precipitation occurred with mercuric sulphate solution; the sulphur compound remained in the filtrate. This was further purified by silver sulphate and barium hydroxide, and the compound obtained from the silver- and barium-free filtrate by fractional crystallisation. From dilute acetone the substance  $C_{11}H_{23}O_4N_2S$  is obtained (10 g.) in white plates or rosettes of indefinite crystalline form. The nitrogen is present as an amino-group; the sulphur does not blacken lead. It was not definitely established that the sulphur was not introduced into the molecule during the preparation. CHEMICAL ABSTRACTS.

**Separation of the Hexone Bases from certain Protein Hydrolysates by Electrolysis.** G. L. FOSTER and CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1923, 56, 545—553).—When the hydrolytic products of casein, fibrin, or red blood-cells are electrolysed in a three-compartment cell, the basic amino-acids, together with about 20% of the non-basic nitrogen, pass into the cathode compartment. By re-electrolysis of the contents of the latter the basic amino-acids may be separated practically completely from the non-basic material. If the reaction of the centre compartment, which contains the protein hydrolysate, is maintained at  $P_H$  5.5, arginine, lysine, and histidine migrate into the cathode compartment in approximately the ratio in which they are present in the hydrolysate. At  $P_H$  7.5, however, only the two former amino-acids are transported, the histidine remaining in the centre compartment. It may be possible to utilise this method for the preparation of histidine. E. S.

**The Blood Pigments. I.** H. FISCHER and K. SCHNELLER (*Z. physiol. Chem.*, 1923, 128, 230—239).—When ethyl 2:4-dimethylpyrrole-3-carboxylate is dissolved in pyridine and acetyl chloride is added, a compound,  $2C_6H_{13}O_2N, C_6H_7N$ , is formed, which crystallises from alcohol in colourless needles, m. p. 173—174°. From 3-acetyl-2:4-dimethylpyrrole, an analogous compound, colourless crystals, m. p. 185°, is obtained, but no satisfactory formula could be assigned to it. From quinoline and ethyl 2:4-dimethylpyrrole-3-carboxylate, colourless needles are obtained, which apparently consist of a mixture of two compounds,  $2C_6H_{13}O_2N, C_6H_7N$  and  $C_6H_{13}O_2N, C_6H_7N$ . These results are considered in relation to the formation of hæmochromogen according to Takayama's method (*Munch. med. Woch.*, 1922, 69, 116). If hæmochromogen is treated with boiling acetic acid containing sodium chloride and hydrochloric acid, hæmin is formed. If mesoporphyrin is treated with ferrous acetate in acetic acid in the absence of oxygen, mesohæmin is formed, although the iron in mesohæmin must be trivalent. A change of valency must take place.

W. O. K.

**Adsorption and Hæmoglobin.** W. E. L. BROWN (*Nature*, 1923, 111, 881—882; cf. this vol., i, 869, 870).—An experiment on the readiness with which the constituents of a mixture of carbon monoxide and oxygen are taken up by hæmoglobin gave results indicating that the union is not due to adsorption. This view is also supported by the fact that the electrical conductivity of gas-free, dialysed hæmoglobin solution is increased by shaking with oxygen or carbon monoxide. The reactions of hæmoglobin with carbon monoxide or oxygen are regarded as being purely chemical.

A. A. E.

**Natural Porphyrins. I. Porphyrin from *Eisenia fetida*.** H. FISCHER and O. SCHAUMANN (*Z. physiol. Chem.*, 1923, 128, 162—166).—A porphyrin has been extracted in very small quantities from earthworms. It crystallises from ether in very fine needles and appears to have the formula  $C_{40}H_{48}O_8N_4$ . Attempts to prepare the methyl ester resulted in a substance having a too small nitrogen content, and giving in acetoacetic acid a spectrum resembling that of acid porphyrin.

W. O. K.

**Natural Porphyrins. II. Turacin.** H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1923, 128, 167—174).—Turacin, a dye isolated from the feathers of certain crested birds, appears from its chemical and spectroscopic properties to be identical with the copper salt of urinoporphyrin.

W. O. K.

**Composition of Thymic Acid.** R. FEULGEN (*Z. physiol. Chem.*, 1923, 128, 154—161).—The question of the isolation of thymic acid (A., 1918, i, 413) is discussed with reference to the views of Thannhauser and Ottenstein (A., 1921, i, 521), and it is concluded that there is no evidence leading to the conclusion that thymic acid is a mixture.

W. O. K.

**The Sugar contained in Tuberculinic Acid, the Nucleic Acid of Tubercle Bacilli.** ELMER B. BROWN and TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1923, 45, 1823—1827).—It is shown that the products of hydrolysis by means of dilute sulphuric acid of tuberculinic acid, purified by the method already given (this vol., i, 160), contain lactic acid and formic acid, and only a relatively small amount of furfuraldehyde. It is therefore evident that the sugar functioning in tuberculinic acid is a hexose. A new analysis for pyrimidines in tuberculinic acid has confirmed results previously reported (*loc. cit.*).  
W. S. N.

**Evidences of a Structure in Gelatin Gels.** R. A. GORTNER and W. F. HOFFMAN (*Proc. Soc. Expt. Biol. Med.*, 1922, 19, 252—253, 257—264).—Gelatin gels of different concentrations, when dried, will again imbibe water according to their original water content and independently of the amount of surface exposed. A 10% gel dried to less than 3% of water content had imbibed at the end of seventy-two hours 6.45 g. of water per g. of dry gelatin, as contrasted with 4.3 g. of water for a 40% gel similarly treated. Gelatin gels have a structure fixed at the time of gelation, and not appreciably altered by drying at room temperature. A crystal structure in which the gelation temperature is actually the m. p. of the crystals would explain the phenomena.

## CHEMICAL ABSTRACTS.

**A Complement of the Amylases.** HANS PRINGSHEIM and WALTER FUCHS (*Ber.*, 1923, 56, [B], 1762—1768).—The term "complement" is applied to an activator of a ferment which differs from the usual co-enzyme in that it is not in nature associated with the ferment and also because it causes the ferment, which is itself active towards a substrate, to become active to a portion of the substrate. Thus the conversion of starch into maltose by means of activated malt extract is generally considered not to proceed beyond the point at which 78% of the starch has undergone saccharification (indications have been obtained during the present work that this limit is rather low). A residual substance is thereby obtained which, under optimal conditions, is only relatively slowly attacked by highly active malt amylase. Addition of yeast which has been treated with toluene, however, so activates the amylase that the "residual substance" is energetically saccharified. In this manner it is possible to obtain maltose in 100% yield from potato or soluble starch.

Two methods are used for the isolation of the "residual substance." Potato starch is fermented by dialysed malt extract in the presence of toluene until about 75% of it has undergone amylolytic fission. The solution is concentrated and submitted to dialysis until the dialysate does not contain fermentable carbohydrate. The remaining solution is concentrated to a small volume and the "residual substance" is precipitated by means of alcohol. Alternatively, the solution obtained after the use of malt extract is heated at 80—90° to ensure destruction of the amylase and subsequently fermented by yeast. The solution is centrifuged

after addition of kieselguhr and dialysed to remove the bulk of the soluble salts. The proteins derived from the yeast are precipitated by addition of colloidal iron hydroxide. The resultant solution is concentrated and precipitated by alcohol. The residual substances obtained by the two methods differ somewhat in their properties, but these differences disappear to a considerable extent on further purification, which is effected by solution in water and reprecipitation by alcohol. The residual substance is a colourless, amorphous powder which is freely soluble in water, but insoluble in organic media. It has  $[\alpha]_D^{25} +160-161^\circ$  in 1% solution,  $[\alpha]_D^{25} +159^\circ$  in 10% solution. It does not give a coloration with iodine.

H. W.

**Nomenclature of the Activity and Affinity of Enzymes.** H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, 56, [B], 1749-1758).—For reasons which are discussed in detail in the original communication, it appears most reasonable to express the activity of enzymic preparations in the manner which has been proposed previously for saccharase and the starch saccharifying enzyme. When  $a.k$  is constant, the expression takes the general form  $\bar{X}f = k + g(\text{substrate})/g$ . (enzyme preparation) or, in the theoretically simplest case in which  $k$  is independent of the concentration of the substrate,  $\bar{X}f = k/g$  (enzyme preparation). In special cases, the limits and conditions of the validity of the relationships are to be indicated. The reaction constants are to be given invariably for optimum acidity and generally for optimal concentration of the activator, preferably at  $18^\circ$ ,  $20^\circ$ , or  $37^\circ$ , so that  $\bar{X}f$  is valid for these temperatures. The expression  $\bar{X}f$  is chosen, in which  $f$  denotes the enzymic faculty of the corresponding enzymic component; for the special enzyme—apart from the terms  $I_f$  and  $S_f$ —the initial letter of the name of the enzyme is adopted if possible (thus, for example,  $U_f$  for urease,  $L_f$  for lipase) or the initial syllable if necessary to avoid confusion (thus  $Kat_f$  instead of  $K_f$  for catalase).

Enzymes are to be characterised further by their affinity constants. The previously proposed expression,  $K_M$  (Michaelis constant), is preferably used as affinity constant and not as dissociation constant, thus  $K_M = (\text{enzyme substrate})/(\text{enzyme}) \times (\text{substrate})$ .  $K_M$  does not appear to vary very greatly with the temperature, but it is nevertheless recommended that the latter should be indicated and chosen in harmony with that adopted in the determination of  $\bar{X}f$ . For saccharase, the values of  $K_M$  vary between 25 and 60; for urease the value is about 90, for a lipase about 15.

H. W.

**Activation of an Enzyme Poisoned by Heavy Metal Salts.** R. A. KEHOE (*J. Lab. Clin. Med.*, 1922, 7, 736-742).—The enzyme in saliva coagulated and inactivated by mercuric chloride and silver nitrate may be reactivated by sufficiently high concentrations of neutral salts of the alkali or alkaline-earth metals; bromides, iodides, and thiocyanates of ammonium, potassium, sodium, strontium, barium, calcium, and magnesium are effective, but not the nitrates, sulphates, citrates, acetates, or carbonates. Re-dissolution of the

precipitate and return (to about 80%) of the starch-splitting activity occurred simultaneously. The enzyme probably consists of, or is intimately associated with, a protein which is soluble and active only when combined with certain salts or metals. Inactivation is ascribed to the formation of insoluble compounds.

## CHEMICAL ABSTRACTS.

**The Purification of Insulin and some of its Properties.** HAROLD WARD DUDLEY (*Biochem. J.*, 1923, **17**, 376—390).—A potent preparation of equal activity to but only about 6% by weight of the crude insulin is prepared by precipitating it as the picrate and converting the insoluble picrate into a soluble hydrochloride by means of alcoholic hydrogen chloride. This preparation does not contain phosphorus and does not give Selivanov's reaction for levulose, or the glyoxylic acid reaction for tryptophan and gives only a very faint and atypical Millon test. On the other hand, the biuret, the Pauly, and the organic sulphur tests are positive. The hydrochloride is precipitated by acids and alkali hydroxides, the former precipitate being more and the latter less potent than the original, and it is destroyed by trypsin and pepsin. Insulin is relatively stable to acid, but is easily decomposed by alkali hydroxides and is rapidly adsorbed in faintly acid solution. It can, however, be filtered without any significant loss through Berkefeld filters if the solution is made weakly alkaline. S. S. Z.

**Effect of Plant Extracts on Blood-sugar.** WILLIAM THALLINER and MARGARET C. PERRY (*Nature*, 1923, **112**, 164—165).—The tentative suggestion is put forward that insulin, which is apparently not itself an oxydase or a peroxydase, indirectly stimulates or activates oxidising ferments in the tissue-cells to action on dextrose, whereas vegetable extracts contain active oxidising ferments and act directly when injected into animals (cf. Winter and Smith, this vol., i, 513, 727; Collip, this vol., i, 728, with whom coincident priority is claimed). A. A. E.

**Glucokinin. A New Hormone Present in Plant-tissue.** J. B. COLLIP (*J. Biol. Chem.*, 1923, **56**, 513—543).—Extracts which have been found to contain a hormone analogous to insulin have been prepared from baker's and brewer's yeast, wheat leaves, onions, lettuce, and the vegetative tissues of other plants. The name *glucokinin* is suggested for this new hormone. Glucokinin has been administered subcutaneously to normal rabbits and to depancreatised dogs. With the former animals there was an initial hyperglycæmia which was followed by a marked hypoglycæmia. In the case of the dogs, the primary effect was an increased rate of excretion of sugar which was followed by a fall in the level of blood-sugar and a decrease in the rate of elimination of sugar. These effects develop more slowly and are maintained for a longer period than in the case of insulin. It is probable that glucokinin plays a rôle in the sugar metabolism of plants similar to that of insulin in animals. E. S.

**A Product of Mild Acid Hydrolysis of Wheat Gliadin.** HUBERT BRADFORD VICKERY (*J. Biol. Chem.*, 1923, 56, 415—428; cf. A., 1922, ii, 754).—Using dilute hydrochloric acid, the author has been unable to obtain conditions whereby the amide groups in gliadin are alone hydrolysed. The hydrolysis of the amide and peptide bonds proceeds simultaneously, although the former are hydrolysed more rapidly. These results do not support the view that hemi- and anti-groups are present in the protein molecule. E. S.

**Chemistry of Vitamin-A. I. Separation of the Active Constituent of Cod-liver Oil, and its Properties.** KATSUMI TAKAHASHI and KOZO KAWAKAMI (*J. Chem. Soc. Japan*, 1923, 44, 580—605).—The authors have attempted to isolate vitamin-A from cod-liver oil and succeeded in obtaining it nearly pure in a semi-crystalline state.

One kg. of cod-liver oil was saponified by warming with 2 litres of alcohol containing 20% potassium hydroxide at 80—90° for thirty minutes. Then 2 litres of 28% alcoholic solution of calcium chloride were gradually mixed with cooling and agitated for one hour. After separation from the calcium soap and potassium chloride, the solution was saturated with carbon dioxide, the solvent distilled off below 60° under reduced pressure, and the residue extracted with ether or light petroleum. The ethereal extract was treated with dilute hydrochloric acid and the fatty acids set free were separated by means of 50% alcohol containing dilute alkali. After drying with sodium sulphate, the solvent was expelled by a current of carbon dioxide, and to the residue about 50 c.c. of 80—90% methyl alcohol were added, and the whole was cooled at 0° for two to three hours, 3—5 g. of cholesterol then separating. More impurities were separated by adding digitonin, and concentrating to a red, viscous syrup, which was once more dissolved in a small quantity of 80—90% methyl alcohol and cooled to -20°, whereby the vitamin-A was separated in the semicrystalline state, the yield being about 0.1%. A mouse dying from lack of vitamin-A recovered completely on taking 0.08 mg. of the substance per day for ten days. The active constituent of butter or egg-yolk has also been isolated by this method.

The isolated constituent contains carbon, hydrogen, and oxygen, but does not contain nitrogen, and seems to be of aldehydic nature. It is very hygroscopic and reduces ammoniacal silver solution, Fehling's solution, and phosphotungstic acid. It is unstable to light and oxygen, and is changed by reduction with hydrogen in the presence of platinum black, but is stable in ether or alcohol, especially in fats. It is insoluble in water, but soluble in alcohol, ether, benzene, acetone, or other organic solvents. In chloroform or carbon tetrachloride solution, it gives the lipochrome reaction and a blue coloration with Japanese acid clay. K. K.

**Observations on the Properties of Arsphenamine (Salvarsan).]** WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, 45, 1807—1817).—Salvarsan (arsphenamine) forms additive compounds with methyl ketones in which the ketone is very firmly

bound (cf. Fargher and Pyman, T., 1920, 117, 372). Neither drying at room temperature or 98° nor reprecipitation from ketone-free methyl alcohol by means of ether removes the ketone. When an aqueous solution containing salvarsan and sodium arsenite is treated with hydrochloric and hypophosphorus acids, a red *polyarsenide* of salvarsan is formed. The velocity of this reaction depends on the method of preparation of the salvarsan, and is apparently greater the less the salvarsan is polymerised. The quantity of hydrochloric acid necessary to precipitate (coagulate) salvarsan from a dilute aqueous solution is constant if the method of preparation does not vary, otherwise varying amounts of acid are necessary. Titration with hydrochloric acid therefore affords a means of determining how closely the routine method of preparation has been followed. In order to obtain a well-coagulated product, in converting salvarsan base into the dihydrochloride, it is advantageous to use a slight excess over the two molecules of hydrochloric acid required.

W. S. N.

**Preparation of New Aromatic Carbonyl Compounds containing Tervalent Arsenic.** OTTO MARGULIES (Brit. Pat. 199091).—Aldehyde- or keto-arsinic acids of the type  $R\cdot AsO_3H_2$  are reduced to the corresponding oxides,  $R\cdot As_2O_3$ , and arseno-compounds,  $R\cdot As\cdot As\cdot R$ , by means of agents (e.g., sodium hyposulphite, phosphorus trichloride, sodium hydrogen sulphite) which reduce the quinquevalent arsenic without affecting the carbonyl groups. [Cf. J.S.C.I., 1923, 42, 861A.]

W. T. K. B.

**Preparation of New Derivatives of Organic Arsenic Compounds.** OTTO MARGULIES (Brit. Pat. 199092).—Aromatic aldehyde- or mixed fatty-aromatic keto-arsinic acids, or the corresponding compounds containing tervalent arsenic (cf. preceding abstract), are treated with hydrazines containing one or more hydrazine groupings (e.g., methylhydrazine, phenylmethylhydrazine, diaminoguanidine). The carbonyl groups are not reduced. The products are mostly well-characterised and crystalline, and possess valuable trypanocidal and spirillicidal properties. W. T. K. B.

**Preparation of New Arsenoxides and Arsenobenzenes.** OTTO MARGULIES (Brit. Pat. 199093).—New organic arsenoxides and arsenobenzenes are obtained from the hydrazones of aromatic aldehyde- or mixed fatty-aromatic keto-arsinic acids or arsenoxides by reduction as described above (preceding abstracts).

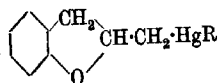
W. T. K. B.

**Magnesium Cumyl Chloride.** L. BERT (*Compt. rend.*, 1923, 177, 195—197).—Cumyl chloride,  $C_6H_5Pr^s\cdot CH_2Cl$ , reacts in ethereal solution with magnesium (previously activated with ethyl bromide) to give a pasty mass of Grignard reagent, and dicumyl (b. p. 350°), a little magnesium remaining undissolved. Decomposition with water affords *p*-cymene, dicumyl, cumyl chloride, and a small quantity of the hydrocarbon described by Errera (A., 1884, 300). The Grignard reagent absorbs oxygen and may thus be converted into cumyl alcohol, b. p. 246° (corr.).

E. E. T.

**Mercury Derivatives of Phenol Ethers.** FRANK C. WHITMORE and EDMUND BURRUS MIDDLETON (*J. Amer. Chem. Soc.*, 1923, 45, 1753—1755).—When boiled in alcoholic solution with potassium iodide or potassium thiocyanate, or when an aqueous solution containing sodium thiosulphate is allowed to remain, *o*-iodomercurianisole and *o*-iodomercuriphenetole give, respectively, *o*-mercury dianisyl and *o*-mercury diphenetyl. The resulting solution is always neutral, but contains inorganic mercury compounds. *o*-Mercury dianisyl and *o*-mercury diphenetyl react normally with alcoholic mercuric chloride, giving quantitative yields of *o*-chloromercurianisole and *o*-chloromercuriphenetole, respectively. *p*-Iodomercuriphenol ethers apparently react with potassium iodide or potassium thiocyanate similarly to the ortho derivatives, but the product is difficult to purify. It is evident that the protection of the phenolic hydroxyl group prevents the fission of the carbon-mercury linking, with formation of alkali, which occurs with mercurated phenols. W. S. N.

**Mercurated 1-Methyl-1 : 2-dihydrobenzofurans.** LINDLEY E. MILLS and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 1842—1854).—The addition of mercuric salts to *o*-allylphenols, and the properties of the mercurated 1-methyl-1 : 2-dihydrobenzofurans (annexed formula) (A., 1922, i, 946),



are shown to be general. Mercuric acetate and mercuric chloride react readily with *o*-allyl-*p*-methylphenol, *o*-allyl-*o*-methylphenol, *m*-hydroxy-*p*-allyltoluene, *p*-bromo-*o*-allylphenol, *p*-carboxy-*o*-allylphenol, *o*-carboxy-*o*-allylphenol, *o*-carbomethoxy-*o*-allylphenol, and *p*-hydroxy-*m*-allylcinnamic acid. The mercurated dihydrobenzofurans undergo the following reactions, in addition to those already reported (*loc. cit.*). The 1-acetoxymercuri- or 1-halogenomercuri-derivatives react with hot concentrated alcoholic potassium cyanide or potassium thiocyanate, to give, respectively, the corresponding 1-cyanomercuri- or 1-thiocyanatomercuri-compounds. The action of warm alcoholic sodium or potassium hydroxide on the 1-chloromercuri-derivatives causes replacement of the chlorine atom by the hydroxyl group; the 1-hydroxymercuri-compounds behave as salt-forming bases, and precipitate insoluble metallic hydroxides, such as cupric hydroxide, from neutral metallic salt solutions. The formation of hydroxymercuri-derivatives in this way is apparently a general reaction, since methylmercuric chloride is converted into methylmercuric hydroxide by a similar procedure. The 1-halogenomercurimethyl-1 : 2-dihydrobenzofurans are converted into metallic mercury and the relevant *o*-allylphenol, by the action of alkaline sodium stannite solution, or of ammonium sulphide, potassium hydrogen sulphide, or hydrogen sulphide in dilute acid solution. By the action of hot, saturated, aqueous sodium thiosulphate solution, they are converted into 1-sodiumthiosulphatomercuri-derivatives, but these are unstable, and readily break down into mercuric sulphide and the *o*-allylphenol. The 1-halogenomercuri-

methyl derivatives do not react with methyl iodide or acetyl chloride.

The following compounds are described. 1-Acetoxymercurimethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 113°; 1-chloromercurimethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 91°; 1-acetoxymercurimethyl-5-methyl-1:2-dihydrobenzofuran, an oil; 1-chloromercurimethyl-5-methyl-1:2-dihydrobenzofuran, m. p. 127.5°; 1-acetoxymercurimethyl-4-methyl-1:2-dihydrobenzofuran, an oil; 1-chloromercurimethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 99.5°; 4-bromo-1-acetoxymercurimethyl-1:2-dihydrobenzofuran, an oil; 4-bromo-1-chloromercurimethyl-1:2-dihydrobenzofuran, m. p. 108°; 1-chloromercurimethyl-1:2-dihydrobenzofuran-6-carboxylic acid, m. p. 200° (decomp.), and its methyl ester, m. p. 107° (decomp.); 1-chloromercurimethyl-1:2-dihydrobenzofuran-4-carboxylic acid, m. p. 212—213° (decomp.), and 1-chloromercurimethyl-4-carboxyvinylene-1:2-dihydrobenzofuran,  $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{H}_2\text{Cl}$ , m. p.

300° (decomp.), are white, crystalline solids, unless otherwise stated. 1-Iodomercurimethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 88°. 1-Iodomercurimethyl-5-methyl-1:2-dihydrobenzofuran, m. p. 131.5°. 1-Iodomercurimethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 94°. 4-Bromo-1-bromomercurimethyl-1:2-dihydrobenzofuran, m. p. 93°. 4-Bromo-1-iodomercurimethyl-1:2-dihydrobenzofuran, m. p. 101°. 1-Hydroxymercurimethyl-1:2-dihydrobenzofuran, m. p. 152°. 1-Hydroxymercurimethyl-6-methyl-1:2-dihydrobenzofuran, a thick oil. 1-Hydroxymercurimethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 149°. 1-Tartrato-di-(mercurimethyl-1:2-dihydrobenzofuran), m. p. 192° (decomp.). 1-Ozalato-di-(mercurimethyl-1:2-dihydrobenzofuran), m. p. 175°. The following three *p*-nitrobenzoates are yellow. 1-*p*-Nitrobenzoatomercurimethyl-1:2-dihydrobenzofuran, m. p. 148°. 1-*p*-Nitrobenzoatomercurimethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 162.5°. 1-*p*-Nitrobenzoatomercurimethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 136.5°. 1-Thiocyanatomercurimethyl-1:2-dihydrobenzofuran, m. p. 112.5°. 1-Cyanomercurimethyl-1:2-dihydrobenzofuran, m. p. 162°. 1-Thiocyanatomercurimethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 102.5°. 1-Cyanomercurimethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 148°. 1-Sodiumthiosulphatomercurimethyl-1:2-dihydrobenzofuran forms glistening, white scales. 1-Sodiumthiosulphatomercurimethyl-4-methyl-1:2-dihydrobenzofuran. 1:1-Mercuridimethylenebis-4-methyl-1:2-dihydrobenzofuran. Methyl *p*-allyloxybenzoate,  $\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$ , glistening, white plates, m. p. 65.5°, is prepared by boiling a mixture of *p*-coumaric acid, allyl bromide, anhydrous potassium carbonate, and acetone. When heated at 230—245°, it undergoes molecular rearrangement, with formation of methyl *p*-hydroxy-*m*-allylcinnamate, which is hydrolysed by means of aqueous sodium hydroxide solution, giving *p*-hydroxy-*m*-allylcinnamic acid,

$\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , white crystals, m. p. 169°, which is used in the preparation of 1-chloromercurimethyl-4-carboxyvinylene-1:2-dihydrobenzofuran.

W. S. N.

**New Organometallic Compounds. Cuprous Phenyl and Silver Phenyl.** RENÉ REICH (*Compt. rend.*, 1923, 177, 322-324).—An ethereal solution of magnesium phenyl bromide dissolves cuprous iodide in the cold, in absence of air, cuprous phenyl, CuPh, being precipitated, after an interval, as a white powder, decomposing at 80°. On warming in benzene solution, diphenyl and a copper mirror result (quantitatively). Cuprous phenyl reacts with water to give benzene and cuprous oxide, with dilute nitric acid to give nitrobenzene, and explodes in presence of the concentrated acid. It decomposes, with blackening, within two days, even in a vacuum.

Cuprous iodide reacts with magnesium ethyl bromide, presumably to give cuprous ethyl, which, however, cannot be isolated, being unstable at temperatures above -18°.

Silver bromide reacts with ethereal magnesium phenyl bromide, the violet solution obtained depositing a yellow precipitate of silver phenyl, AgPh. The preparation is effected in darkness, and the product decomposes in ethereal suspension at -18° in a few hours, to give silver and diphenyl. It is highly explosive.

E. E. T.

### Physiological Chemistry.

**Effect of Insulin on the Respiratory Exchange.** H. W. DUDLEY, P. P. LAIDLAW, J. W. TREVAN, and E. M. BOOCK (*Proc. Physiol. Soc., J. Physiol.* 1923, 57, xlvii-xlix).—Two independent investigations, by the first two and last two authors, show that although sugar disappears from the blood, the injection of insulin does not produce its effect by directly increasing the rate of combustion of glucose. Experiments by the first-named author further show that the disappearance is not due to an increased glycogen storage in the liver.

G. B.

**The Distribution of Inorganic Phosphate of the Blood between Plasma and Cells.** T. F. ZUCKER and M. B. GUTMAN (*Proc. Soc. Expt. Biol. Med.*, 1921, 19, 169-171).—By working rapidly with the Bell and Doisy method, the inorganic phosphate found in the plasma is the same as that of whole blood. If the colorimetric reading is made within half an hour after the blood is drawn, the distribution is equal; if one hour elapses, the whole blood contains more than the plasma; after several hours the difference is still greater. Phosphate-ions freely permeate the cell-wall, and are stored as organic, acid-soluble phosphate; the latter in turn is readily hydrolysed when there is need of phosphate in the plasma.

CHEMICAL ABSTRACTS.

**The Calcium Content of the Blood of Thyroidectomised Animals.** MARIE PARRON (*Endocrinology*, 1923, 7, 311-312).—The blood of thyroidectomised sheep contained a smaller amount

of calcium than normal, supporting the idea that one of the most important functions of the thyroid is the regulation of calcium metabolism.

CHEMICAL ABSTRACTS.

**Distribution of Sugar in Whole Blood, Plasma, and Corpuscles; Permeability of Red-blood Corpuscles for Sugar in Diabetic and Non-diabetic Cases.** H. J. JOHN (*Arch. Intern. Med.*, 1923, 31, 555—566).—In the blood drawn from non-diabetic persons in the course of dextrose tolerance tests, the concentration of dextrose in plasma and corpuscles was nearly the same, whereas in diabetic blood obtained under the same conditions the concentration in the plasma was always greater. The difference was not due to relative impermeability of the diabetic corpuscles to dextrose, for when exposed for two hours to a 1% dextrose solution, these took up more dextrose than did non-diabetic corpuscles similarly exposed.

CHEMICAL ABSTRACTS.

**The Nature of the Sugar in Blood.** J. A. HEWITT (*Brit. Med. J.*, 1923, I, 590—591).—Objections are raised to the technique employed by Cooper and Walter and by Winter and Smith, and it is asserted that no evidence exists that  $\gamma$ -dextrose is a component of normal blood; neither are theories of diabetes mellitus which are dependent on the presence of  $\gamma$ -dextrose securely based. It is, however, admitted that  $\gamma$ -dextrose may have a transient existence, and may perhaps be regarded as an intermediate product in the katabolism of dextrose.

A. A. E.

**The Blood Content in Various Animals of Sugar, Residual Nitrogen, Carbamide Nitrogen, Creatinine Compounds, and Uric Acid by Folin's Methods.** ARTHUR SCHEUNERT and HERTHA VON PELCHRZIM (*Biochem. Z.*, 1923, 139, 17—29).—A table is given summarising the values found for the constituents of blood mentioned in the title for a variety of vertebrates—dog, sheep, ox, horse, pig, birds, and fish. As a rule the physiological limits of variation of these constituents are the same in all the animals including man. Uric acid was, however, not found in the blood of dogs, sheep, oxen, horses, pigs, or fishes, but that found in birds agreed in content approximately with that of man.

H. K.

**The Uric Acid Content of the Blood of Various Animals.** KONSTANZE SCHMITT-KRAHMER (*Biochem. Z.*, 1923, 139, 30—33).—In view of the results of Scheunert and von Pelchrzim (previous abstract) on the absence of uric acid from the blood of various animals and thus contrary to the results of some other workers, the method of Folin as modified by Pucher and with further slight modifications has again been applied to the blood of various animals containing added known amounts of sodium urate. In all cases, the uric acid found corresponded with that added except in birds, where the excess corresponded with the values found by Scheunert and von Pelchrzim.

H. K.

**The Influence of the Normal Working Journey on the Composition of the Blood of the Horse.** ARTHUR SCHREUNERT and M. BARTSCH (*Biochem. Z.*, 1923, 139, 34—37).—The content of sugar, residual nitrogen, carbamide nitrogen, creatine, and creatinine of the blood of a horse performing its daily work was the same as during rest; the capacity for combining with carbon dioxide of the plasma was, however, as a rule depressed. H. K.

**The Relation of the Individual Organs to Blood Clotting.** KEIZO HIRUMA (*Biochem. Z.*, 1923, 139, 152—187).—Ligature of the pancreatic ducts in rabbits leads to an enormous increase of fibrinogen in the blood whilst the thrombin content is unchanged. Parallel with this increase in fibrinogen there is a prolonged delay in blood clotting. Thrombin can be stored unimpaired in the frozen condition for some weeks. Its action is rapidly destroyed by shaking serum but is intensified by passage of carbon dioxide.

H. K.

**The Physico-chemical Bases of Vital Permeability.** I and II. R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1923, 139, 261—269, 270—273).—I. The normally observed impermeability of a collodion membrane for hæmoglobin is not due to the narrowness of the pores, because capillary-active substances such as sodium oleate, linolate, glycocholate, digitonin, and Witte peptone render the collodion permeable to hæmoglobin. This is a reversible condition of the pores. As a working hypothesis the view is adopted that only the positively adsorbed substances can enter the capillaries with the water and pass through.

II. A collodion membrane impermeable to hæmoglobin is rendered permeable by treatment with atropine, pilocarpine, caffeine, strychnine, quinine, and morphine, but not by codeine. Cocaine and novocaine have no action.

H. K.

**The Swelling of Blood-corpuscles and Hæmolysis.** KLOTHILDE GOLLWITZER-MEIER (*Biochem. Z.*, 1923, 139, 86—113).—Washed blood-corpuscles of man, when suspended in various isosmotic salt solutions and submitted to increasing tensions of carbon dioxide, undergo swelling and hæmolysis. The swelling is favoured by anions in the order  $\text{Cl} > \text{NO}_3 > \text{SO}_4$  and by cations in the order  $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$ . For hæmolysis, however, a different order is observed,  $\text{NO}_3 > \text{Cl} > \text{SO}_4$  and  $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$ . Corpuscles washed with small quantities of isosmotic dextrose or sucrose solutions show little agglutination, but with increased carbon dioxide tension there is progressively increasing agglutination, sedimentation, and hæmolysis. Suspensions of corpuscles rotated in a tonometer undergo spontaneous hæmolysis attributable to electrokinetic processes.

H. K.

**Placental Transmission. I. The Calcium and Magnesium Content of Fœtal and Maternal Blood-serum.** L. JEAN BOGERT and E. D. PLASS (*J. Biol. Chem.*, 1923, 56, 297—307).—At the time of birth, the calcium content of the serum of the fetus is

higher than that of the mother; the value for the former is usually higher, and that of the latter lower, than the normal value. No difference was observed in the magnesium content; in both cases, this showed a tendency to fall below the normal value. E. S.

**Placental Transmission. II. The Various Phosphoric Acid Compounds in Maternal and Fœtal Serum.** E. D. PLASS and EDNA H. TOMPKINS (*J. Biol. Chem.*, 1923, 56, 309—317).—A comparison has been made between the distribution of phosphoric acid in maternal and fœtal serum at the time of birth. Lipoid phosphoric acid is present only in small quantities in fœtal blood, whilst its content is above the normal in the blood of the mother. The value for inorganic phosphoric acid is low in the serum of the mother and high in that of the fœtus. There is also a tendency for organic phosphoric acid to be higher in the serum of the fœtus than in that of the mother. The total phosphoric acid content is greater in maternal than in fœtal serum. E. S.

**The Inhibitory Effect of Blood-serum on Hæmolysis.** ERIC PONDER (*Proc. Roy. Soc.*, 1923, [B], 95, 42—61).—Hæmolysis of red blood cells by saponin or by sodium taurocholate is inhibited by serum protein. A quantitative study has been made of this effect. The degree of inhibition is measured in terms of the amount of hæmolysing agent used up by the protein. The inhibitory effect of serum is shown to be approximately constant for sera from different animals belonging to one species and to be constant from day to day, but to change if the serum be dried or exposed to air. The quantity of hæmolytic substance neutralised per unit of serum decreases with increase in the concentration of serum, and the general conclusion is drawn that the inhibition is due to the formation of a loose adsorption compound. Hæmoglobin inhibits in a way similar to that of serum protein. W. O. K.

**Influence of Pyramidone on Metabolism.** HANS GESSLER (*Arch. expt. Path. Pharm.*, 1923, 98, 257—287).—Administration of pyramidone to patients with fever causes a reduction in heat production, a retention of water and of sodium chloride, and, apparently, a diminution in the destruction of body proteins. E. S.

**The Calcium and Phosphoric Acid Metabolism of the Horse when Normally Fed.** ARTHUR SCHEUNERT, ADOLF CHATTKA, and MARTA WEISE (*Biochem. Z.*, 1923, 139, 1—9).—For horse receiving a daily ration of oats, hay, and chopped straw, the daily intake was 25.5 g. CaO and 53.2 g.  $P_2O_5$ . Over an experimental period of thirteen days during which daily analyses were made of urine and faeces, the total unexcreted CaO for thirteen days was 56.0 g. and  $P_2O_5$  148.5 g. In another horse, however, fed on oats and hay the daily intake was CaO 16.1 g., and  $P_2O_5$  36.5 g. and over ten-day period of observation the total unexcreted CaO over ten days was 3.5 g. whilst the  $P_2O_5$  balanced. The conclusion is drawn that observations over too short periods are liable to lead to wrong conclusions. H. K.

**The Influence of Exclusive Oat Feeding on the Calcium and Phosphoric Acid Metabolism of the Horse.** ARTHUR SCHEUNERT, ADOLF SCHATTKER, and MARTA WEISE (*Biochem. Z.*, 1923, 139, 10—16).—Exclusive feeding of a horse on oats (a diet rich in phosphates but poor in calcium) over a period of ten days showed a surplus excretion of 83.9 g. of CaO, but an approximate  $P_2O_5$  equilibrium. The same was observed in another horse fed initially on oats, hay, and chopped straw, when the hay was omitted. A rich phosphate diet poor in calcium can therefore extract calcium from the depots of the fully-grown horse.

H. K.

**The Calcium Balance.** ADOLF SINDLER (*Pflüger's Archiv*, 1922, 197, 386—403; from *Chem. Zentr.*, 1923, i, 859).—Two feeding experiments in three periods with growing individuals showed that the calcium balance depends on the supply of meat. The calcium balance is more favourably affected by a decrease in the meat ration than by addition of calcium chloride. In the latter case, the first retention of calcium is followed by its elimination by the kidneys and intestines. Loss in phosphorus consequent on administration of calcium was not observed, but rather an improvement of the phosphorus balance. Increased compensatory retention of potassium and increased excretion of sodium was also observed. The magnesium balance appears to depend on several factors.

G. W. R.

**The Influence of the Phosphate-ion on Carbohydrate Metabolism. I.** H. ELIAS and A. LÖW (*Biochem. Z.*, 1923, 138, 279—283).—Perfusion of surviving livers of frogs with Ringer solution containing phosphate and dextrose shows that glycogen is not stored, but is, on the contrary, mobilised. The fall of blood-sugar in cases of hyperglycæmia by administration of phosphates does not therefore appear to be due to storage of glycogen.

H. K.

**The Influence of the Phosphate-ion on Carbohydrate Metabolism. II.** H. ELIAS, C. POPESCU-INOTESTI, and C. ST. RADOSLAV (*Biochem. Z.*, 1923, 138, 284—293).—Intravenously administered hypertonic mono- or di-sodium phosphates depresses the blood-sugar content of dogs and rabbits in small doses. Larger doses lead to a hyperglycæmia in the rabbit, but in the dog to a protracted hypoglycæmia.

H. K.

**The Influence of the Phosphate-ion on Carbohydrate Metabolism. III.** H. ELIAS, C. POPESCU-INOTESTI, and C. ST. RADOSLAV (*Biochem. Z.*, 1923, 138, 294—298).—In dogs and rabbits the hyperglycæmia produced by adrenaline is depressed by phosphate injections.

H. K.

**The Influence of the Phosphate-ion on Carbohydrate Metabolism. IV.** H. ELIAS, C. POPESCU-INOTESTI, and C. ST. RADOSLAV (*Biochem. Z.*, 1923, 138, 299—306).—Intravenous doses of phosphate which are without action on the blood-sugar content of normal dogs depress the hyperglycæmia and glycosuria of dogs with extirpated pancreas.

H. K.

**Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen.** A. V. HILL and HARTLEY LUPTON (*Quart. J. Med.*, 1923, 16, 135—170).—Oxygen is not used in the primary breakdown processes of rest or activity; it is used only in recovery processes. Large amounts of lactic acid, up to 1.5 g. per kg. body weight, may be produced. If exercise is too great the supply of oxygen cannot cope with the production of lactic acid and exhaustion results. The exhaustion following long continued moderate exercise is due to the diffusion of lactic acid out of the muscles where it is slowly oxidised and removed. Lactic acid in the body always appears as the lactate of sodium, potassium, or ammonium. The rate at which chemical processes of recovery occur starts at a low level, rises to a maximum, and slowly falls to zero. The greater the initial effort the greater is the relative rate of recovery.

CHEMICAL ABSTRACTS.

**Carbamide as a Protein Substitute for Ruminants.** F. HONCAMP and E. SCHNELLER (*Biochem. Z.*, 1923, 138, 461—496).—Metabolism experiments were carried out on two wethers fed on a standard diet with and without the addition of carbamide. The nitrogen content of the faeces shows little change, but in one wether a protein sparing action of the carbamide was observed, and in the other almost all the carbamide was excreted in the urine. On a protein-deficient diet containing copious carbohydrate, carbamide promotes storage of protein. The substitution of casein for carbamide led to a greater storage of nitrogen. H. K.

**The Life-supporting Action of the Leguminous Tribe.** L. BECKZELLER and A. BILLIG (*Biochem. Z.*, 1923, 139, 225—228).—White rats fed exclusively on the broad bean (*Vicia faba*) live fifteen or twenty times longer than when fed on the haricot bean. H. K.

**The Nutritive Value of Fats and Lipoids. II. Nutritive Value of Fatty Acids and Glycerol in their Combined and Incombined States.** KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1923, 44, 547—573).—The nutritive value of six pure fatty acids, stearic, palmitic, oleic, decolic, lauric, and myristic acids, and of the corresponding triglycerides in presence and absence of vitamin-A was investigated by means of feeding experiments on mice. Tables and curves of the results are given, and may be summarised as follows: (1) In like conditions, free fatty acids have less nutritive value than the corresponding glycerides. (2) In the presence of a small quantity of vitamin-A, the nutritive value of the fatty acids increases as the molecular weight of the acids decreases and the same is the case with the corresponding glycerides. The higher acids, such as palmitic and stearic acids, are bad as food, but stearic is better than oleic acid. (3) By supplying a sufficient quantity of vitamin-A, mice grow normally with food in which fatty acids are present in the form of triglycerides but not if they are in the free state. The effect on the growth of each glyceride is almost the same. (4) Vitamin-A has no direct effect on the digestion and absorption of fats. (5) It is improbable that fats are

absorbed after complete decomposition into fatty acids and glycerol in the digestive organs. (5) Animals fed with a large quantity of free acids (stearic, palmitic, etc.) become less resistant to disease and are apt to develop diseases of the respiratory organs, especially pneumonia.

K. K.

**Nutritive Value of Fats and Lipoids. III. Are Carbohydrates and Fats Necessary as the Food of Animals?** KIRSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1923, 44, 574—589).—As already stated by Funk ("The Vitamines," p. 346), vitamin-B has an intimate connexion with the metabolism of carbohydrates. When carbohydrates are ingested without vitamin-B, they have an injurious effect on the nutrition of animals. In general, unlike proteins, vitamins, and salts, fats and carbohydrates are not to be regarded as absolutely necessary elements of nutrition, but merely as auxiliary sources of energy.

K. K.

**The Phosphorus Metabolism of the Nervous System. I.** ELISABETH HECKER and HANS WINTERSTEIN (*Z. physiol. Chem.*, 1923, 128, 302—316).—Estimations made by Bloor's nephelometric method of the phosphorus content of the brain and of the cerebrospinal cord of the frog show that the latter contains twice as much phosphorus as the former and that the upper half of the spinal cord contains less than the lower.

W. O. K.

**The Content of the Normal Human Cerebrospinal Fluid in Phosphates and Sulphates.** FELIX HAUBOWITZ (*Z. physiol. Chem.*, 1923, 128, 290—301).—The normal human cerebrospinal fluid contains on the average 0.0018% of phosphorus and 0.0011% of sulphur. These values are fairly constant for different cerebrospinal fluids and are less than the corresponding values for the blood. The phosphorus is almost completely inorganic, whilst about one-fifth of the sulphur is in combination in protein.

W. O. K.

**Metabolism of the Surviving Mammalian Heart.** FELIX KLEWITZ (*Arch. exp. Path. Pharm.*, 1923, 98, 91—105).—Perfusion experiments have been made with surviving hearts from normal dogs and rabbits and also from animals the glycogen supply of which had been depleted by hunger and injection of phloridzin. The results indicate that, in all probability, the surviving heart can utilise fats and nitrogenous substances, in addition to carbohydrates, as sources of energy. Further, when nitrogenous substances (amino-acids) are added to the perfusion fluid, these may be retained by the heart probably both as a reserve supply of energy and to replace wasted tissue. Creatine and creatinine are formed in varying quantities by surviving hearts.

E. S.

**The Effect of Insulin on the Glycogen in the Tissues of Normal Animals.** HAROLD WARD DUDLEY and GUY FREDERIC MARRIAN (*Biochem. J.*, 1923, 17, 435—438).—The sugar which disappears from the blood of normal animals under the influence of insulin is neither converted into nor stored as glycogen either in the liver or in the skeletal muscles. The glycogen in these two tissues

disappears almost completely when a dose of insulin which is sufficient to cause hypoglycæmic convulsions is administered. No evidence could be found that carbohydrate is converted into fat in normal animals on administration of insulin. S. S. Z.

**Unsaponifiable Matters (Higher Alcohols) in Shark and Ray-liver Oils. II.** YOSHIYUKI TOYAMA (*J. Chem. Ind. Japan*, 1923, 26, 37—48; cf. *ibid.*, 1922, 25, 1).—The unsaponifiable matter of the liver oil of *Chlamydoselachus anguineus*, Garman, is mainly composed of oleic alcohol. Small amounts of cetyl alcohol and of cholesterol were also found, but neither selachyl alcohol nor batyl alcohol could be detected. It also contains an appreciable amount of squalene and a minute quantity of a saturated hydrocarbon. The unsaponifiable matters of the liver oils of (1) *Scymnorhinus licha*, (2) *Centroscyllium ritteri*, (3) *Hypranchias deani*, (4) *Galeocerdo tigrinus*, and (5) two commercial shark-liver oils contained large amounts of selachyl alcohol,  $C_{20}H_{40}O_3$ , and of batyl alcohol,  $C_{26}H_{52}O_3$ . Squalene was found in those of (1), (2), and (5). K. K.

**Presence of Sucrase in the Walls of the Ovarian Mucoid Cysts.** P. LECÈNE and H. BERRY (*Compt. rend.*, 1923, 177, 222—224).—By macerating the walls of ovarian mucoid cysts with water in presence of toluene and thymol, the authors obtained a solution which fermented sucrose, indicating the presence of a sucrase. Morphological analogy probably exists between the tissue examined and the lining of the foetal intestine, for which a sucrase is the characteristic enzyme. E. E. T.

**The Function of the Parathyroids.** HARALD A. SALVENSEN (*J. Biol. Chem.*, 1923, 56, 443—456).—Parathyroidectomised dogs have been maintained alive for about two years by administration of calcium salts either intravenously in the form of calcium chloride, or orally in the form of milk or of soluble calcium salts. During this time, the animals were in a state of "latent tetany"; cessation of the administration of calcium salts always produced tetany. During latent tetany, the calcium content of the blood is below, and that of the inorganic phosphoric acid above, the normal. The appearance of tetany is always accompanied by a decrease, and its disappearance by an increase in the calcium content of the blood. During latent tetany, and more so during tetany, there is a lowered tolerance for sugar which is due to a functional disturbance of the glycogen-forming organs. These results are in agreement with the view put forward by MacCallum and Voegtlin (*J. Expt. Med.*, 1909, 11, 118), and subsequently abandoned, that the symptoms of parathyroid insufficiency are due to calcium deficiency. E. S.

**Creatine Formation during Tonic Muscle Contraction.** K. UYENO and T. MITSUDA (*J. Physiol.*, 1923, 57, 313—317).—In male toads and frogs, creatine was found to increase in the clasp muscles during coupling in the breeding season. Decerebrate rigidity in cats also increases the creatine in the rigid muscles in accordance with the results of Pchel'haring and van Hoogenhuyze

(A., 1910, ii, 324), but contrary to those of Dusser de Barenne and Terveart (*Pflüger's Archiv*, 1922, 195, 370).

The carnosine content of muscle is, on the other hand, not influenced by rigidity. G. B.

**Creatine Formation in Frog's Muscle Contracted by Nicotine.** T. MITSUDA and K. UYENO (*J. Physiol.*, 1923, 57, 280—286).—The authors confirm the older results of Pekelharing (A., 1911, ii, 1115) that the contracted muscles contain more creatine than the normal; the increase is something like 5—10% of the total amount in the muscle. G. B.

**The Pigment Question.** B. BRAHN and M. SCHMIDTMANN (*Arch. path. Anat. Physiol.*, 1922, 239, 488—490; from *Physiol. Abstr.*, 1923, 8, 199).—The brown pigment which may be extracted from myocardium which has undergone brown atrophy cannot be distinguished from melanin. The wide variation in the published analysis of melanin indicates that this is not a single substance, but a group of substances with similar properties. The pigment of brown atrophy is, like melanin, iron-free and contains sulphur and phosphoric acid. Its rather sparing solubility in alcohol does not indicate a non-melanin nature, as melanin varies considerably in this respect, becoming decreasingly soluble with age. For the present, human endogenous pigments are to be divided into two classes, those derived from hæmoglobin, and the autochthonous pigments or melanins. W. O. K.

**Pigment of Human Skin.** G. O. E. LIGNAC (*Arch. path. Anat. Physiol.*, 1922, 240, 383—416; from *Physiol. Abstr.*, 1923, 8, 228).—Four stages in human skin pigmentation can be distinguished. First there is formed a parent substance, a prepigment sensitive to light, and reducing silver nitrate. From this is derived, by oxidation and polymerisation, a melanin which still reduces silver nitrate but is bleached only by active oxygen. It is possible that the prepigment is an *o*- or *p*-dihydrobenzene derivative and that melanin is produced by the oxidation of quinonoid substances. Strong oxidation of melanin brings about the third stage. A yellow pigment which will not reduce silver nitrate is formed. This pigment can be obtained by the action of hydrogen peroxide. In the body, it has been observed only in the skin lymph nodes. The fourth phase includes only the colourless decomposition products of melanin. There is no sufficient ground for assuming the presence of oxidising or other enzymes in the skin. Radiation with ultra-violet light leads to a primary pigmentation and secondary depigmentation, in which hydrogen peroxide may be concerned. W. O. K.

**The Phosphorus Content of Pathological Melanin.** O. SALKOWSKI (*Arch. path. Anat. Physiol.*, 1922, 240, 353—355; from *Physiol. Abstr.*, 1923, 8, 199).—Melanin from melanotic livers contained 0.99% and 0.71% of phosphorus in two cases. Phosphorus was found in the examination of another melanotic liver melanin. Brown pigment from a brown atrophied heart contained 0.18% of

phosphorus. The significance of this small amount with respect to the nature of the pigment of the brown heart is doubtful. Other investigators have found 0.50% of phosphorus in the pigment of the brown heart.

W. O. K.

**Iron Reaction in Malarial Pigment.** E. MAYER (*Arch. path. Anat. Physiol.*, 1922, 240, 117—126; from *Physiol. Abstr.*, 1923, 8, 199).—Although the usual microchemical reactions do not show the presence of iron in malaria pigment, iron can be demonstrated by certain modifications in which it is brought gradually into solution and made to react with reagents at the same time. This is achieved by staining with Berlin-blue in which aqueous hydrochloric acid is replaced by 2—5% alcoholic hydrochloric acid, in which the malaria pigment is slowly solidified, or with the Hueck modification of the Turnbull-blue reaction. In this method, the ammonium sulphide is allowed to act until the pigment begins to dissolve. The use of these methods confirms Seyfarth's finding of iron in malaria parasites. The finding of blue haloes indicates that the iron split from the pigment diffuses to the boundaries of the pigment containing cells. Occasionally blue or green globules of malaria pigment are seen with this technique. Formalin pigment does not give the iron reaction with this method, which can accordingly be used for differential diagnosis.

W. O. K.

**The so-called Lipofuscin.** O. LUBARSCH (*Arch. path. Anat. Physiol.*, 1922, 239, 491—503; from *Physiol. Abstr.*, 1923, 8, 199).—The evidence at hand indicates that lipofuscin is a mixture of pigment and fat. The designation "lipofuscin" and the distinction from melanin of the substance designated is not warranted. It is true that physiological melanin is formed in ectodermal cells. Lipofuscin is not limited to ectodermal cells, although it is found there chiefly. It is not known whether its rare occurrence in connective-tissue is to be attributed to its formation or to its deposition there. The author distinguishes three endogenous pigments: (1) the hæmoglobinogenous; (2) the proteinogenous, including "lipofuscin"; and (3) the lipoidogenous, including only the true lipochromes.

W. O. K.

**Some Derivatives of "Saccharin."** A. F. HOLLEMAN (*Rec. trav. chim.*, 1923, 42, 839—845).—A discussion of the connexion between taste and constitution. A résumé of most of the work done on this subject is given. It is shown that benzene disulphimide has a very sweet taste, but much less than "saccharin," and in addition it has a bitter after-taste; "6-chlorosaccharin" is about half as sweet as "saccharin." The imide of quinoieinic acid is sour, whilst phthalimide is tasteless and quinoieic acid is acidic.

J. F. S.

**The Formation of Lactose in the Lacteal Gland. The rôle of Leucine.** ERICH HESSE (*Biochem. Z.*, 1923, 138, 441—460).—The observation of Röhmnn that addition of leucine greatly accelerates the formation of lactose in the sterile maceration juice of the lacteal gland of the cow has been followed up. By fraction-

ation of the osazones, maltosazone has been isolated. Attention is directed to Fischer's opinion that lactose could possibly arise out of maltose by a stereochemical change.

H. K.

**The Reduction of Methylene-blue by Iron Compounds.** EDWARD JAMES MORGAN and JUDA HIRSCH QUASTEL (*Proc. Roy. Soc.*, 1923, [B], 95, 61—71).—Boiled milk to which ferrous sulphate has been added will reduce methylene-blue. The effect is shown to be due entirely to the mineral constituents of the milk, as methylene-blue is reduced by ferrous sulphate in the presence of sodium hydroxide, carbonate, hydrogen carbonate, or phosphate, and of the sodium salts of various organic acids such as acetic, tartaric, or citric, two molecules of ferrous sulphate being required to reduce one of methylene-blue. This effect seems to depend on the low ionisation of ferric hydroxide, that is, on the high affinity of the ferric-ion for the hydroxyl-ion.

W. O. K.

**Action of Alcoholic Extracts of Pancreas (Insulin) on the Critical Glycæmia.** H. CHABANIER, C. LOBO-ONELL, and M. LEBERT (*Bull. Soc. Chim. biol.*, 1923, 5, 389—397).—Mainly a confirmation of results obtained by McLeod and his collaborators.

E. S.

**The Action of Insulin in Glycæmia and Acidosis.** A. DESGREZ, H. BERRY, and F. RATHERY (*Compt. rend.*, 1923, 176, 1833—1836).—Insulin in the form of powder, as prepared by a series of fractional precipitations, is to be preferred to the simple extracts of the active substance. The latter exert a characteristic toxicity in addition to their effect on glycæmia. Analyses are quoted showing the marked effect exerted by stated doses of insulin in diminishing the excretion of sugars, ketones, and  $\beta$ -hydroxy-butyric acid. The suggestion is made that the metabolism of these substances is probably conditioned by certain tautomeric forms of dextrose.

H. J. E.

**Use of Yeast Extracts in Diabetes.** L. B. WINTER and W. SMITH (*Nature*, 1923, 112, 205; cf. this vol., i, 513, 727).—The variability of the activity of the extract from different samples of yeast is confirmed, and it is noted that micro-organisms other than yeast can also yield substances which reduce the concentration of the blood-sugar.

A. A. E.

**Tetany.** S. G. Ross (*Can. Med. Assoc. J.*, 1923, 13, 97—103).—In four cases of tetany (three gastric, the fourth mercuric chloride poisoning), the sodium and chloride content of the blood were reduced, the hydrogen carbonate increased, the calcium normal, and the inorganic phosphorus increased in two cases. In a case of mercuric chloride poisoning with acute nephritis but no tetany, the sodium and chloride content were low, the hydrogen carbonate and calcium normal, and the phosphorus high.

CHEMICAL ABSTRACTS.

**Derivatives of Phenylarsinic Acid (Quinquevalent Arsenic) in Treatment of Experimental Trypanosomiasis and Spirillosis. Relation between the Therapeutic Action of the Aromatic Arsinic Acids and their Constitution.** E. FOURNEAU, A. NAVARRO-MARTIN, and M. and MME. TRÉFOUEL (*Ann. Inst. Pasteur*, 1923, 37, 551—617).—A very large number of previously known derivatives of phenylarsinic acid,  $C_6H_5\cdot AsO_3H_2$ , have been prepared and examined with regard to their maximum tolerated dose, and their effective curative dose in animals infected with trypanosomes or spirochaetes. Brief accounts of the chemical methods used in preparing the compounds are given.

W. O. K.

**The Analysis of the Pharmacological Action of Nitrous Oxide.** HEINRICH BART (*Biochem. Z.*, 1923, 139, 114—138).—Contrary to Wieland's results, the author finds that nitrous oxide acts as a true lipid-soluble narcotic. Experiments were carried out on frogs at various temperatures between 3° and 25° with air, hydrogen, nitrogen, and nitrous oxide, and with various mixtures with oxygen, on tadpoles and worms and some anaërobes, as, for example, ascarids.

H. K.

**The Pharmacology of Potassium- and Calcium-ions.** M. ROSENMANN (*Z. ges. exp. Med.*, 1922, 29, 334; from *Physiol. Abstr.*, 1923, 8, 202).—Investigation of the action of adrenaline, pilocarpine, ergotoxin, etc., on various muscular processes in the presence and absence of calcium- and potassium-ions tends to show that the action of calcium is chiefly stimulant, whilst that of potassium is chiefly paralyzant. Calcium in the presence of adrenaline shows an exaggerated paralyzant action.

W. O. K.

**Lævulose, Dextrose, and Galactose Tolerance in Dogs.** MEYER BODANSKY (*J. Biol. Chem.*, 1923, 56, 387—393).—The ingestion of lævulose is less effective than that of dextrose in producing a rise in blood-sugar. In agreement with the results of Foster (this vol., i, 503), and in opposition to those of Folin and Berglund (A., 1922, i, 487), galactose has been found to produce a marked hyperglycæmia. This, however, is prevented if sufficient dextrose is present in the circulation. The reducing substances excreted in the urine following the ingestion of lævulose and galactose do not consist of these sugars.

E. S.

**[Physiological] Action of Homologous Aliphatic Quaternary Ammonium Bases.** FRITZ KÜLZ (*Arch. exp. Path. Pharm.*, 1923, 98, 339—369).—A comparison has been made of the physiological actions of the quaternary salts comprised in the two general series trimethylalkylammonium iodide and triethylalkylammonium iodide. The curare action of the two series does not run parallel. In the trimethyl series, the activity decreases from the lowest member to that containing a propyl group; the butyl derivative

has ten times the activity of the propyl derivative; thereafter the activity increases slowly as the series is ascended. In the triethyl series, the first two members have approximately the same activity; succeeding members show a regular increase. The curve of activity of each series is, in general, the reciprocal of the curve of solubility of the corresponding perchlorates. The action of the various members of the two series on the vagus nerve and on skeletal muscle has also been determined.

E. S.

**The Relations between Constitution and [Physiological] Action in Alicyclic Tetrahydro- $\beta$ -naphthylamine and its Derivatives.** II. M. CLOETTA and E. WASER (*Arch. exp. Path. Pharm.*, 1923, 98, 198—220).—The authors have previously shown (A., 1913, i, 1280) that the physiological action (dilation of the pupils and rise in body temperature and blood pressure) of tetrahydro- $\beta$ -naphthylamine is not modified qualitatively by the introduction of one methyl group into the amino-group. When, however, two methyl groups are introduced, such a modification does occur. Thus, the dimethyl derivative causes a fall in blood pressure and dilation of the pupils, but is without action on the body temperature. The corresponding methochloride has an action intermediate between that of the mono- and di-methyl derivatives. It produces a rise in blood pressure, dilation of the pupil, and is without action on the body temperature; in addition, it has a curare-like action. This quaternary salt, like 2-amino-methyl-*ac*-tetrahydro- $\beta$ -naphthalene, differs from the other derivatives which produce a rise in blood pressure in that successive injections are equally effective in their action. The observation made previously (*loc. cit.*), that the introduction of an acid group into the amino-group of tetrahydro- $\beta$ -naphthylamine reverses the action of this substance, has been found to hold for other groups. Thus, injections of the carbamic ester and of the ethylthiocarbamido-, phenylcarbamido-, phenylthiocarbamido-, and even of the tetrahydro- $\beta$ -naphthylthiocarbamido- derivatives of tetrahydro- $\beta$ -naphthylamine cause none of the effects produced by the free base. When the distance of the amino-group from the aromatic nucleus is increased, as in aminomethyltetrahydro- $\beta$ -naphthalene, no essential difference in the action is produced; when it is decreased, as in  $\alpha$ -hydrindamine, the action is considerably diminished.

E. S.

**Detoxication of Cyanides in Health and Disease.** MEYER BODANSKY and MOISE D. LEVY (*Arch. Int. Med.*, 1923, 31, 373—389).—A study of the excretion of thiocyanate in the saliva before and after the ingestion of potassium cyanide or thiocyanate by normal and diseased persons. The latter excreted less thiocyanate than the former, but the increases after ingestion of potassium cyanide and thiocyanate were somewhat greater. It appears that in certain diseases, such as pellagra, the cyanide detoxifying power remains unimpaired, provided the supply of cystine is adequate.

CHEMICAL ABSTRACTS.

**Comparison of the [Physiological] Actions of *d*-, *l*-, and *i*-Camphor. V. Electrographical Investigation on Isolated Frog's Hearts.** G. JOACHIMOGLU and E. MOSLER (*Arch. expt. Path. Pharm.*, 1923, **98**, 1—11).—The same physiological action was produced by the three enantiomorphs, thus confirming results obtained by other means (A., 1917, i, 528; 1921, i, 146). E. S.

## Chemistry of Vegetable Physiology and Agriculture.

**Protein Synthesis by *Azotobacter*.** O. W. HUNTER (*J. Agric. Res.*, 1923, **24**, 263—274).—Dried *Azotobacter* cells containing 11.8% protein were obtained by culture on solid media, whereas those from an aerated liquid culture had a protein content of 30%. Within the limits of the experiment, the yield of cells increased with the amount of sugar in the medium, and the nitrogen fixed was generally of the order 16—17 mg. per g. of dextrose consumed. In media containing molasses, *Azotobacter* converted soluble nitrogenous substances into more complex proteins, and at the same time utilised the molasses as a source of energy for nitrogen fixation. The addition of straw to the media did not cause any appreciable increase in the quantity of nitrogen fixed.

A. G. P.

**The Propionic Acid Fermentation of Lactose.** J. M. SHERMAN and R. H. SHAW (*J. Biol. Chem.*, 1923, **56**, 695—700).—The accelerating effect which certain other organisms have on the production of propionic acid by *Bacterium acidipropionici* (d) (*J. Gen. Physiol.*, 1921, **3**, 657) is not due to the production of lactic acid from the lactose by these organisms.

E. S.

**The Production of Tyrosine by a Putrefactive Anaërobe.** S. C. HALL and F. FINNERUD (*Proc. Soc. Expt. Biol. Med.*, 1921, **19**, 48—50).—Certain anaërobes, as *Bacillus bifementans*, *B. centrosporogenes*, and *B. histolyticus*, when grown in deep brain medium, ground meat, salmon, milk, or suspended casein, form tyrosine. The medium must not contain an excess of monosaccharides.

CHEMICAL ABSTRACTS.

**Lactic Acid Fermentation of Dextrose by Peptone.** CHR. BARTHEL and H. VON EULER (*Z. physiol. Chem.*, 1923, **128**, 257—283).—The experiments of Schlatter (A., 1922, i, 1096), who has claimed that he has demonstrated the lactic acid fermentation of dextrose by peptone, have been repeated with negative results, provided that the conditions were aseptic. Where fermentation with production of lactic acid set in, bacterial contamination could be shown.

W. O. K.

**Fat Metabolism of the Timothy Grass Bacillus.**  
**II. The Carbon Balance-sheet and Respiratory Quotient.**  
 MARJORY STEPHENSON and MARGARET DAMPIER WHETHAM  
 (*Proc. Roy. Soc.*, 1923, [B], 95, 200—206; cf. A., 1922, i, 500).—The carbon balance of timothy grass bacillus, grown in a culture medium containing dextrose as source of carbon, was studied. The carbon was completely accounted for by the carbon dioxide formed, the carbon in the organism, and the carbon remaining in the culture medium after filtration. The longer the duration of the experiment, the more carbon dioxide is produced from the reserve lipid of the bacillus. The respiratory quotient is greater than unity in the earlier part of the experiment when synthesis of lipid and protein is taking place. Afterwards, when the dextrose is consumed, the respiratory quotient sinks below unity.  
 G. W. R.

**Does the Introduction of an Ethoxyl Group into Aromatic Compounds Increase their Bactericidal Action on the *Pneumococcus* and the *Gonococcus*?** A. D. HIRSCHFELDER and L. J. PANKOW (*Proc. Soc. Expt. Biol. Med.*, 1921, 19, 64—67).—The introduction of an ethyl group into substances like sodium phenol-sulphonate and sodium salicylate or *p*-aminophenol and *p*-nitrophenol does not cause increased bactericidal action.

#### CHEMICAL ABSTRACTS.

**The Influence of the Medium on the Toxicity of certain Alkaloids towards Protozoa.** T. A. HENRY and H. C. BROWN (*Trans. Roy. Soc. Trop. Med.*, 1923, 17, 61—71).—Quinine, emetine, and conessine are much more toxic to protozoa when in an alkaline medium. There would appear to be a specific toxic action of the alkaloid followed by some secondary action of the alkali. The uses of this observation in the alkaloidal treatment of protozoal diseases are noted.  
 A. G. P.

**Volutin and Nucleic Acid in Various Yeasts.** M. GLAUBITZ (*Biochem. Z.*, 1923, 139, 77—85).—By staining the volutin granules in a variety of *Torula* and distillery yeasts with methylene-blue followed by dilute acid (Meyer) and the nucleic acid by methylene-blue followed by phosphine, an attempt has been made to determine whether volutin and nucleic acid are identical. The staining reactions were found insufficient to decide. In all cases, nucleic acid appeared to be present to a lesser extent than volutin. There is no relation between baking capacity and volutin content. For *Torula* yeasts the greater the reproductive capacity the greater the nucleic acid content.  
 H. K.

**Action of Yeast on Calcium Lactate: Production of Ethyl Alcohol.** E. KAYSER (*Compt. rend.*, 1923, 176, 1662—1665).—The addition of various types of yeast to solutions of calcium lactate containing those inorganic substances which would be associated with the yeast under natural conditions results in the production of pyruvic, acetic, and valeric acids, together with aliphatic alcohols. The rate of action varies with the type of

yeast used, is more rapid at 28° than at 12°, and takes place to a greater extent at the surface than in the body of the solution. It increases with concentration of calcium lactate, and is most marked in the presence of potassium dihydrogen phosphate and of ammonium phosphate. The production of pyruvic acid is favoured by the addition of calcium carbonate. Small quantities of ethyl valerate and amyl acetate were also obtained in most of the experiments, the amount depending on the experimental conditions.

H. J. E.

**Phytochemical Reductions. XVII. Partial Reduction of Dinitro-compounds.** CARL NEUBERG and ELSA REINFURTH (*Biochem. Z.*, 1923, 138, 561—568).—*m*-Dinitrobenzene, when added in alcoholic solution to an actively fermenting surface yeast in the presence of sucrose or starch syrup, becomes reduced to *m*-nitroaniline and *m*-dinitroazoxybenzene. An intermediate product in the formation of the latter is probably *m*-nitrophenyl-hydroxylamine as the solutions at an intermediate stage showed the methemoglobin reaction.

H. K.

**The Nitrogenous Bases in the Mycelium of *Aspergillus niger*.** W. VORREDDT (*Bull. acad. polon. sci. let.; classe sci. math. nat.*, 1921, [B], 223—236; from *Physiol. Abstr.*, 1923, 8, 208).—From 1400 g. of dry mycelium the following were obtained: adenine (0.7 g.), xanthine, guanine, cytosine (0.3 g.), choline (0.4 g.), lysine (0.6 g.); ammonia, arginine, and histidine were not found. It is thought that the relatively high content of free bases indicates that these are intermediate products in the synthesis of proteins and not catabolic products.

W. O. K.

**Chemistry of the Higher Fungi. XVII. *Amanita muscaria*, L., *Inoloma albiviolaceum*, Pers., *Boletus Satanas*, Lenz., and *Hydnum versipelle*.** LUCIE BARD and JULIUS ZELLNER (*Monatsh.*, 1923, 44, 9—17).—*Amanita muscaria* contains a colloidal substance, viscosin (cf. A., 1918, i, 55), and a readily soluble substance, mycetid. The former, on hydrolysis, affords dextrose and methyl-pentoses, but no mannose or galactose; the latter affords dextrose and other sugars. Hydrolysis of the fungus membrane gives dextrose, pentoses, methylpentoses (the two latter being formed from the more readily hydrolysed portion of the parent polysaccharide) and glucosamine (produced with difficulty by the hydrolysis of a chitin-like parent substance).

*Inoloma albiviolaceum* contains oleic and palmitic acids (together with derived fats), lecithins (?), mycose, dextrose, choline (?), and a mixture of substances resembling ergosterol and cerebrin.

*Boletus Satanas*, known to contain mannitol and mycose, also contains palmitic acid and derived fats, unsaturated acids of the oleic and linoleic type (oxidation of the mixture of acids, with permanganate, affording a dihydroxystearic acid, m. p. 135°, and stearic acid, m. p. 173°), ergosterol, m. p. 164° (identical with that found in ergot and toadstools), a substance resembling cerebrin and one resembling a phlobaphen, mannitol, choline, muscarine, and potassium chloride.

*Hydnum versipelle* contains a resin [easily hydrolysed, giving amorphous acids and resembling one previously isolated (A., 1915, i, 1086)], a substance resembling ergosterol, mannitol, dextrose, and choline. The aqueous extract of the fungus contains carbohydrates, which, on hydrolysis, afford dextrose, pentoses, and methylpentoses.

E. E. T.

**Plant Respiration and Photosynthesis.** H. A. SPOHR and J. M. MCGEE (*Carnegie Inst. Pub.*, 1923, 325, 1-98).—Interdependence may exist between photosynthesis and respiration. In the plant-cell, the carbohydrates and fats serve as the fundamental sources of energy in respiration; carbohydrates act as protein-sparers. The leaves of *Helianthus annuus* contain more amino-acid (which accumulates in the dark, the protein diminishing) and less carbohydrate than the stems. Amino-acids have stimulating effects on certain enzymes; they stimulate cells to metabolise more food material. An attempt to explain this on the basis of the isomerisation of dextrose to more rapidly metabolised isomerides gave negative results. Whilst *laevulose* metabolises more rapidly than dextrose, and shows relatively high respiratory activity, it depressed the activity of leaves when amino-acids were given. For the determination of the rate of respiration, an electrometric method was employed to estimate the carbon dioxide; the amino-acids were estimated by Van Slyke's micro-method, and the sugars by the author's method (A., 1921, ii, 715). Deleano's statement (*Jahrb. wiss. Bot.*, 1921, 51, 552) that the nitrous acid method of estimating amino-groups is untrustworthy in the presence of carbohydrates and nitrates was not confirmed. A plant of *Helianthus annuus* showed a gradual increase in the rate of respiration during the first forty-eight hours, the amino-acids probably having a stimulating action, compensating for the diminishing carbohydrate content, whilst with excised leaves the rate decreases up to the forty-eighth hour, when there is a slight increase. There is a gradual depletion of carbohydrates and increase in amino-acid content, but the stem and roots show a slight decrease in amino-acid content. In excised leaves, the carbohydrate content decreases and that of the amino-acid increases. Excised leaves, when placed in the dark in a nitrogen-free nutrient solution containing 7% of dextrose, take up sugar and store it, and show an increased content of amino-nitrogen. Amino-acids are produced in the dark and accelerate the rate of carbohydrate consumption. Leaves fed on aminoacetic acid solution (for example) showed increased respiratory activity and rate of sugar consumption, whereas leaves fed on dextrose maintained an almost constant sugar content, but the amino-acid content increased three-fold, the rate of respiration decreasing for thirty hours, then increasing for fifty hours to a value slightly above the original. With leaves of the Canada Wonder bean, where the carbohydrate and amino-acid content increased during the experiment, the rate of respiration after falling to a minimum at the end of thirty-five hours rose to about the original value; the minimum marks the point

when the amino-acids have accumulated in a quantity sufficient to influence respiration. When the leaves are fed with amino-acids in addition to sugar the rise in the rate of respiration is continuous. The use of sucrose leads to similar results, but the influence of amino-acids was not observed with levulose. There was a great increase in amino-acid content and respiratory activity when it was fed to the leaf, but aminoacetic acid gave very little additional stimulation. A natural accumulation of amino-acids resulting when excised leaves are kept in the dark is as effective as artificial addition in stimulating respiratory activity. The rate of respiration has no direct relation to the carbohydrate supply. Light affects the carbohydrate and amino-acid content in opposite ways, decreasing the latter. Neither nitrate nor ammonia accumulates in leaves kept in the dark for ninety-five hours. The existence of an internal factor is postulated for cases in which the photosynthetic activity varies independently of external conditions. Whilst the chlorophyll content regulates the degree of photosynthetic activity in leaves poor in chlorophyll, the limiting factor in leaves rich in chlorophyll is this internal factor, which resembles an enzyme in its behaviour and is responsive to variation of temperature. The fact that reduced pressure and narcosis inhibit photosynthesis as well as respiration supports the view that a chemical or energetic relationship exists between the two processes. A molecular relation between photosynthesis and respiration depends on the activity of the intermediate products of sugar katabolism which act as "building blocks" with carbon dioxide or some of the primary products of its photochemical breakdown; this would account for asymmetric synthesis. Differential estimations of carbon dioxide showed, in the cases of leaves of the sunflower and Canadian Wonder bean, that the rate of photosynthesis of a leaf, the store of carbohydrates of which has been greatly depleted, is initially low and rises with continued exposure to light, the rate of respiration also increasing. Leaves previously kept in the dark show a continuous decrease in respiratory activity and a declining photosynthesis. This also holds for high concentrations of carbon dioxide, i.e., respiration parallels carbon dioxide fixation. Photosynthesis may be a dual or coupled reaction.

CHEMICAL ABSTRACTS.

**Influence of the Concentration of Organic Substances on the Formation of Starch in Vegetable Cells.** A. MAIGE (*Compt. rend. Soc. Biol.*, 1922, 86, 856—857; from *Physiol. Abstr.*, 1923, 8, 209).—Increase of sugar and water in the cell leads to increased starch formation.

W. O. K.

**Influence of the Nature of Organic Substances of the Formation of Starch in Vegetable Cells.** A. MAIGE (*Compt. rend. Soc. Biol.*, 1922, 87, 303—304; from *Physiol. Abstr.*, 1923, 8, 209).—Bean embryos without cotyledons were cultivated on 5 to 10% solutions of different sugars and the formation of starch observed. The amount of starch formed is held to depend on the penetrability

of the sugar except in cases where there is a definite toxic action, as with mannose and particularly with galactose. W. O. K.

**Chemical Composition of Protoplasm of Plasmodium.** W. W. LEFESCHKIN (*Ber. deut. bot. Ges.*, 1923, 41, 179—187).—An examination of the protoplasm from plasmodia of *Fuligo varia* gave the following results. Dry matter 17.4%. In the dry matter, the water-soluble material, amounting to 40.7%, principally from the vacuoles, consists of monosaccharides, 14.2%; proteins, 2.2%, and amino-acids, purine bases, asparagine, etc., 24.3%. The material insoluble in water, 59.3%, forming the ground mass of the protoplasm, consists of nucleoproteins, 32.3%; nucleic acids, 2.5%; globulin, 0.5%; lipoproteins (plasmatin), 4.8%; neutral fats, 6.8%; phytosterol, 3.2%; phosphatides, 1.3%; other organic substances (polysaccharides, colouring matter, resin), 3.5%; ash constituents, 4.4%. G. W. R.

**Comparative Plant Chemistry. V. *Alchemilla Alpina*, L.** HANS VOGL (*Monatsh.*, 1923, 44, 19—28).—The stems and leaves of this plant were found to contain an optically inactive hydrocarbon,  $C_{23}H_{38}$ , hexagonal plates, m. p. 70°, oleic and linoleic acids (in roughly equal amounts), a little combined phosphoric acid (lecithin?), and a dextrorotatory, white, amorphous substance,  $C_{10}H_{16}O_3$ , m. p. 268° (decomp.) (if not treated previously with alkali) or 253° (decomp.) (if alkali is used in its purification). This substance may be a resin-ester, which would account for the m. p. results. From the sample of m. p. 253°, no crystalline derivatives could be obtained. Short heating with acetic anhydride gave an acetyl derivative, m. p. 164°, prolonged heating, one melting at 138°. Nitric acid in glacial acetic acid solution gave a nitro-derivative, m. p. 206°. In addition to the above substances, the stems and leaves contain a phlobaphen and tannins (of two types), choline, phenolic compounds, dextrose, and lævulose (these two in the proportion of 4:1). Extraction with water revealed the presence of inorganic matter and of carbohydrates, which, on hydrolysis, gave a little galactose, considerable quantities of pentoses, but no dextrose or mannose. The total ash (from stem and leaf) was 7.03%.

A brief examination of *Alchemilla Alpina* root (mainly rhizomes) showed that alkaloids were absent. Very little of the above hydrocarbon was present, whereas the leaves, etc., contained 1—2%. A resin-substance, similar to that described above, was isolated, and was soluble in alkali. Tannins of the protocatechuic type were found in large quantities, and also dextrose and lævulose (in this case in the proportion 2:1). The total root extract was about 60% greater than the leaf extract (per cent.). What medicinal effect is possessed by the root can only be attributed to the tannins present. E. E. T.

**Constituents of the Wax-like Coating on the Surface of the Apple.** CHARLES E. SANDO (*J. Biol. Chem.*, 1923, 56, 457—468).—Dried apple skins were extracted successively with light petroleum

and ether. Fractionation of the light petroleum extract yielded triacontane,  $C_{30}H_{62}$ , heptacosanol,  $C_{27}H_{56}O$  (cf. Kipping, T., 1893, 53, 452), and a number of crystalline products which could not be identified owing to the small yield. Heptacosanol has not previously been isolated from natural sources. From the ether extract, a new alcohol,  $C_{30}H_{60}O$ , prismatic needles, m. p. 284—285°, was isolated. The name *malol* is suggested for this. Malol is dextrorotatory, exhibits mutarotation, and appears to be the lower homologue of the isomeric alcohols oleanol and prunol isolated by Power and Tutin (T., 1908, 93, 891) and by Power and Moore (T., 1910, 97, 1099), respectively. It gives the Liebermann-Salkowski reaction for cholesterol, forms a crystalline sodium salt,  $C_{30}H_{59}O_2Na$ , and a diacetyl derivative,  $C_{30}H_{56}O_4Ac_2$ , needles, m. p. 199—200° (decomp.), which, when dissolved in 70% alcohol and boiled for two hours, is converted into the monoacetyl derivative,  $C_{30}H_{58}O_3Ac$ , small needles, m. p. about 279—281° (decomp.). Methylmalol,  $C_{30}H_{58}O_3Me$ , m. p. 170.5—171.5° after sintering at 110°; and acetylmethylmalol,  $C_{30}H_{56}O_3MeAc$ , m. p. 243—244°, have also been prepared. E. S.

The Chemical Contents of *Polygonum hydropiper*. JAN BIELECKI and DAWID LIBERMAN (*1<sup>st</sup> Zjazd Chemików Polskich*, 1923, 60—61). Whilst certain colour reactions seem to point to the presence of alkaloidal substances in *Polygonum hydropiper*, no alkaloid was isolated from the alcoholic or acid extracts, although the latter were found to contain certain organic acids, of which only gallic acid was identified. An extract of *P. hydropiper* made with lime water gave on distillation with steam and extraction with ether a small quantity of green oil, from which crystals of a characteristic odour separated, which gave many reactions for alkaloids. R. T.

A New Essential Oil from the Seeds of *Sium latifolium*, L. G. V. FIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 296—303).—The crushed seeds of the umbelliferous plant, *Sium latifolium*, L., yield about 6% of an essential oil, a typical sample of which has  $d_{20}^{25}$  0.8533,  $[\alpha]_D^{25} +77.24^\circ$ ,  $[\alpha]_D^{25} +98.40^\circ$ ,  $[\alpha]_D^{25} +127.24^\circ$ ,  $[\alpha]_D^{25} 163.80^\circ$ ,  $[\alpha]_D^{25}/[\alpha]_D^{25} 1.99$ . Fractionation of the oil shows that it contains about 80% of *d*-limonene, which was identified by means of its tetrabromide. The higher boiling fraction appears to consist of a ketone, giving an *oxime*, m. p. 101—102°,  $[\alpha]_D^{25} +136.76^\circ$ ; the ketone, although having an odour reminiscent of carvone, is not identical with the latter. The oil prepared from unripe seeds has similar properties to the above.

In character, the oil is similar to oil of caraway, which is also composed of two main constituents, but contains a much higher proportion of ketone. The structure of the seeds was compared with that of caraway seeds, and it was found that the resin ducts of the former were much nearer the endosperm than those of caraway. It is thought possible that hydrocarbons are formed in the ducts lying nearer the endosperm, whilst oxygenated compounds

are produced in the outer portion of the seed; the difference of structure would thus account for the difference in character of the essential oils in the two plants.

G. A. R. K.

**Estimation of Adsorbed Bases in Soils and the Importance of these Bases in Soil Economy.** D. J. HISSINK (*Soil Sci.*, 1923, 15, 269—276).—Twenty-five g. of soil (50 g. of sandy loams) are shaken in a beaker with 100 c.c. of a warm normal solution of sodium chloride and filtered into a litre flask. The soil on the filter is treated with successive portions of the sodium chloride solution until the flask is filled to the mark. Each portion of solution is allowed to pass through the filter before the addition of the next. The washing is repeated until a second litre of filtrate is obtained. The difference in calcium content of the two separate litres of filtrate corresponds with replaced calcium. For adsorbed potassium and magnesium, a similar method is employed, preferably using a 25 g. soil sample and normal ammonium chloride solution for leaching. Of the adsorbed ions calcium was the most preponderant, smaller proportions of the total potassium, magnesium, and sodium being adsorbed.

A. G. P.

**The Soil Solution and its Importance in the Growth of Plants.** N. M. TULAIOV (*Soil Sci.*, 1923, 15, 229—234).—The relationship between the osmotic pressure of the soil solution and plant growth is investigated. An increased osmotic pressure delayed the germination of seeds, weakened the seedlings, and arrested the growth of the plant in all its stages. There is an optimum osmotic pressure for plant growth. Increased osmotic pressure increased the total crop yield up to an optimum figure, after which there was a decline in yield. An increased osmotic pressure produced an increased nitrogen content in the crop, and greater hardness of grain.

A. G. P.

**The Question of Obtaining the Soil Solution.** N. M. TULAIOV and M. S. KUZMIN (*Soil Sci.*, 1923, 15, 235—239).—Soil is packed in the annular space between a metal cylinder and an inner cylinder of metallic net covered on the outward (soil) side with filtering muslin. Pressure is applied to the soil surface by an ordinary turn-screw press and the inner cylinder is evacuated. The soil solution can be extracted in about fifteen minutes. Consecutive samples of soil solution showed identical chemical constitution and osmotic pressures. Considerable amounts of soil solutions may be obtained in this way even when the moisture content is low.

A. G. P.

## Organic Chemistry.

**Genesis of Hydrocarbons.** R. D'ANDRIMONT (*J. Inst. Petr. Tech.*, 1923, 9, 287—291).—A brief general discussion on the genesis of hydrocarbons (petroleum) and their localisation in certain zones in the earth's crust. Whether from accumulations of vegetable and animal remains the processes of organic transformation give rise to coal or hydrocarbons depends on: (1) the proportion of cellulose to fatty matter; (2) the conditions of deposition; and (3) pressure, temperature, and time. The most favourable situation for the third of these conditions is in the fractured zones bordering mountain folding.  
L. J. S.

**Studies in Mutual Solubility. I. Introductory. The Mutual Solubility of Glycerol and Aliphatic and Aromatic Ketones.** BASIL CHARLES McEWEN (*T.*, 1923, 123, 2279—2284).

**Studies in Mutual Solubility. II. The Mutual Solubility of Glycerol and Alcohols, Aldehydes, Phenols, and their Derivatives.** BASIL CHARLES McEWEN (*T.*, 1923, 123, 2284—2288).

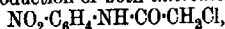
**The Alkylglycerols.** R. DELABY (*Ann. Chim.*, 1923, [ix], 19, 275—326).—A more detailed description of work previously published (cf. this vol., i, 84, 85, 289, 531, 646; ii, 264).  
H. J. E.

**Ethylation with Ethyl Sulphate.** A. R. CADE (*Chem. and Met. Eng.*, 1923, 29, 319—323).—Ethyl sulphate is a satisfactory general ethylating agent for the preparation of ethyl ethers, esters, amines, and imides. If the reagents employed be nearly dry both ethyl groups react; if there be a large amount of water present only one group reacts completely. A temperature of 100—150° is usually optimal, but reaction occurs even at room temperatures. Aromatic and aliphatic ethers are both prepared as with methyl sulphate in presence of an alkali. Amines are mono- and di-ethylated according to the conditions of reaction; both ethyl groups can be caused to react if an alkali be present. Imides and acids are best treated in the form of their alkali salts. Being non-inflammable, non-toxic, non-corrosive, and of low volatility, besides being available in large quantities and in a high degree of purity, ethyl sulphate should find a wide chemical use, especially as it reacts without application of pressure.  
T. S. W.

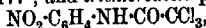
**The Colloidal Electrolyte extracted from Carrageen** (*Chondrus Crispus*). FRANK COURTNEY HARWOOD (*T.*, 1923, 23, 2254—2258).

**Bromination of Aliphatic Acids.** BRIAN DUNCAN SHAW (*T.*, 1923, 123, 2233—2240).

**Direct Conversion of Derivatives of Dichloroacetic Acid into Derivatives of Trichloroacetic Acid.** ALVIN S. WHEELER and SAMUEL C. SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 1994—1998).—*o*-Toluidine dichloroacetate, prisms, m. p. 140°, is formed when equimolecular proportions of *o*-toluidine and dichloroacetic acid react in ice-cold carbon tetrachloride solution; *p*-toluidine dichloroacetate is prepared similarly, and has m. p. 160° (Baralis, *Res. chim. med. farm.*, 2, 301, gives m. p. 140°). Aniline trichloroacetate, m. p. 163° (Beamer and Clarke, A., 1897, i, 785, give m. p. 145°), is obtained by the action of excess of dichloroacetic acid or trichloroacetic acid on aniline, without cooling, or by the interaction of aniline and trichloroacetic acid at -3° in carbon tetrachloride solution. *o*-Toluidine trichloroacetate, colourless plates, m. p. 167—168° (decomp.), *p*-toluidine trichloroacetate, m. p. 135° (Baralis, *loc. cit.*, gives m. p. 137°),  $\alpha$ -naphthylamine trichloroacetate, pale violet plates, m. p. 173° (decomp.), and *m*-nitroaniline trichloroacetate, pale yellow plates, m. p. 147°, are prepared by similar methods. It is evident that the formation of these derivatives of trichloroacetic acid from dichloroacetic acid must be preceded by a rearrangement of 2 mols. of the latter, giving 1 mol. of chloroacetic acid and 1 mol. of trichloroacetic acid. This view is substantiated by the production of both chloroaceto-*p*-nitroanilide,



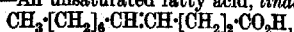
yellow prisms, m. p. 177°, and trichloroaceto-*p*-nitroanilide,



pale yellow, prismatic needles, m. p. 140°, when *p*-nitroaniline and dichloroacetic acid are warmed together, the product being then heated at 100° with phosphoric oxide. The identity of these anilides is confirmed by their direct synthesis from chloroacetic acid, or trichloroacetic acid, and *p*-nitroaniline. W. S. N.

**The Oxidation of Stearic Acid and Related Compounds by Oxygen.** ERNST ZERNER (*Naturprodukte*, 1923, 83—94).—The higher fatty acids and related compounds are slowly oxidised by atmospheric oxygen in presence of a catalyst of the type of manganese stearate at 130° with formation of a variety of products. The oxidation is accompanied by a steady rise in the acid and saponification numbers and, in the case of unsaturated substances such as oleic acid, by a fall in the iodine number. A detailed study was made of the oxidation of stearic acid. The product obtained after oxidising for thirty-one hours formed a soap which lathered well but could not be salted out, indicating the presence of hydroxyl groups. It contained unsaponifiable matter which had the composition of an alcohol,  $\text{C}_{14}\text{H}_{30}\text{O}$ , and as identifiable products succinic, pimelic, and heptic acids, and in the distillate carried forward with the oxygen current, the lower fatty acids down to formic acid and an alcohol,  $\text{C}_{12}\text{H}_{26}\text{O}$ . When ethyl stearate was oxidised in the same way, the rate of disappearance of the ethoxyl group did not indicate that one end of the chain was being attacked preferentially. Compounds containing as few as eight carbon atoms in a chain are not oxidised under the above conditions. E. H. R.

**Constitution and some Properties of an Unsaturated Fatty Acid,  $C_{15}H_{23}O_2$ , isolated from *Lindera obtusiloba*.** YOSHITORA IWAMOTO (*J. Chem. Ind. Japan*, 1923, 26, 708—716; cf. *ibid.*, 1921, 24, 1114).—An unsaturated fatty acid, *linderic acid*,



a light yellow oil, was isolated from the oil obtained from *Lindera obtusiloba*, B.L. It has m. p. 1.0—1.5°,  $d_4^{20}$  0.92461,  $n_D^{20}$  1.44922,  $n_D^{25}$  1.45113, iodine value 126.33, neutralisation value 282.26. The methyl ester has b. p. 123—125°. Treated by Hazara's oxidation method, the acid gave *dihydroxylinderic acid*,  $C_{15}H_{22}O_4(OH)_2$ , slender needles, m. p. 102°. The original acid was ozonised and decomposed with hot water; from the decomposition products, succinic and *n*-octoic acids and *n*-octaldehyde were isolated. K. K.

**Linoleic Acid and its Anhydride.** D. HOLDE and S. WEILL (*Chem. Umschau*, 1923, 30, 205—206).—A sample of linoleic acid prepared by Grün and Schönfeld from poppy-seed oil (*Z. angew. Chem.*, 1910, 29, 47) was investigated and gave the following mean characters: iodine value (Hanus), 178.6; acid value, 196.7;  $d_4^{20}$  0.9025;  $n_D^{20}$  1.4711; m. p. -25° to -24°. The anhydride was prepared by boiling for seven hours with acetic anhydride and distilling off the excess of acetic anhydride and the acetic acid formed under reduced pressure. The residue was freed from unchanged linoleic acid by dissolving in light petroleum, treating with 5% sodium hydroxide solution, removing the soap with 50% alcohol and finally with water, and distilling off the light petroleum in a current of carbon dioxide under reduced pressure. The yield was 85—92% of the theoretical. When the light petroleum solution was cooled to -75° the anhydride was precipitated as a fine white precipitate, of which the melting point was, however, not sharp enough to be determined. H. C. R.

**Hongay Oil [from the Seeds of *Pongamia glabra*, Vent.].** R. D. DESAI, J. J. SUDBOROUGH, and H. E. WATSON (*J. Ind. Inst. Sci.*, 1923, 6, 93—110).—The fatty acids present as glycerides include myristic (0.23%), palmitic (6.06%), stearic (2.19%), arachidic (4.30%), lignoceric (3.22%), dihydroxystearic (4.36%), linolenic (0.46%), linoleic (9.72%), and oleic (61.30%) acids. There is 3.56% of unsaponifiable matter, which contains brassicasterol and sitosterol together with an oil of high refractive index. [*Cf. J.S.C.I.*, 1923, Oct.] H. C. R.

**Cashew Kernel Oil [from the Seeds of *Anacardium occidentale*, Linn.].** C. K. PATEL, J. J. SUDBOROUGH, and H. E. WATSON (*J. Ind. Inst. Sci.*, 1923, 6, 111—129).—The oil comprises glycerides of oleic (73.8%), linoleic (7.7%), palmitic (6.4%), stearic (11.2%), and lignoceric (0.5%) acids together with 0.42% of unsaponifiable matter consisting mainly of sitosterol. [*Cf. J.S.C.I.*, 1923, Oct.] H. C. R.

**Preparation of Malono-*p*-ethoxyanilic Acid and its Esters.** AKTEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 371692; from *Chem. Zentr.*, 1923, ii, 1089).—*p*-Phenetidine is treated with

a large excess of ethyl malonate. After removal of the excess of ethyl malonate, the product of reaction is treated with a dilute solution of an alkali hydroxide. The formation of the diphenetide,  $\text{CH}_3(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , in large quantities is prevented by using large excess of ethyl malonate. Thus from ethyl malonate and *p*-phenetidine in the proportion of 7:1, four parts of *ethyl malono-p-ethoxyanilate*,  $\text{CH}_3(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , are formed, together with one part of the diphenetide. After removal of excess of ethyl malonate and treatment with potassium hydroxide, *malono-p-ethoxyanilic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is obtained by treatment of the potassium salt with hydrochloric acid.

G. W. R.

**Crystalline Structure of Anhydrous Racemic Acid.** W. T. ASTBURY (*Proc. Roy. Soc.*, 1923, [A], 104, 219—235).—From observations made with an X-ray spectrometer the crystalline structure of racemic acid has been deduced. The crystallographic cell is associated with only 1 mol. of tartaric acid ( $\text{C}_4\text{H}_4\text{O}_6$ ) and is not the true fundamental cell. The fundamental cell is associated with 1 mol. of *d*-tartaric acid and 1 mol. of *l*-tartaric acid. There is no evidence from X-ray examination that racemic acid exists as an independent inactive doublet of molecular weight 300. The chemical molecule in racemic acid is substantially of the same shape and dimensions as the molecule in tartaric acid. A small contraction in the length of the molecule and the absence of a certain cleavage is associated with small changes in physical properties which accompany the formation of racemic acid from its active components. The disappearance of the distortion of the hydroxyl groups of tartaric acid is favourable to the hypothesis of the anomalous optical properties of the active acid. An explanation is given of the multiple twinning and irregular growth of anhydrous racemic acid.

J. F. S.

**Dithioformic Acid.** T. G. LEVI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 569—572).—The author has prepared various derivatives of dithioformic acid from the potassium salt obtained by treating chloroform with potassium sulphide (cf. Cambi, A., 1909, i, 646) in alcoholic solution under definite conditions.

The silver,  $\text{H}\cdot\text{CS}_2\text{Ag}$ , and lead salts,  $(\text{H}\cdot\text{CS}_2)_2\text{Pb}$ , were obtained as orange-yellow precipitates, but could not be prepared quite pure owing to their insolubility in ordinary organic solvents; both are comparatively stable, the former blackening at 95—100° and the latter at 130—135°. The zinc salt is yellowish-white and the cobalt salt deep brownish-red.

The disulphide,  $(\text{H}\cdot\text{CS}\cdot\text{S}\cdot\text{S}\cdot\text{CS}\cdot\text{H})_2$ , obtained as a yellowish-red precipitate by cautious oxidation of the potassium salt in alcoholic solution by means of iodine, decomposes at above 200° into carbon disulphide, hydrogen sulphide, carbon, and sulphur. T. H. P.

**Photochemical Production of Formaldehyde.** E. C. C. BALY, I. M. HEILBRON, and W. F. BARKER (*Nature*, 1923, 112, 323; cf. T., 1921, 119, 1025, and Spoeher, this vol., ii, 452).—Further experiments confirm the previous observation that form-

aldehyde is formed by the action of ultra-violet light of short wave-length on aqueous solutions of carbon dioxide. Spoehr's failure to observe the formation of formaldehyde may be due to deterioration of the quartz mercury lamp employed. The method of procedure adopted by the authors is described in detail.

A. A. E.

**The Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. II. The Action of Ozone on Ethylene.** E. W. BLAIR and T. S. WHEELER (*J. Soc. Chem. Ind.*, 1923, 42, 343—350r).—Experiments on the action of ozone on ethylene were made both by ozonising a mixture of ethylene and oxygen and by the direct action of ozonised oxygen or air on ethylene in presence and absence of water or ammonia. The resulting gas was then washed with water and the solution analysed for formic acid, dissolved ozone, hydrogen peroxide, and formaldehyde. The primary product of reaction of the gases at the ordinary temperature is the ozonide  $C_2H_4O_3$ , which may then decompose in various ways. When mixtures of dry oxygen and ethylene were ozonised there was much carbon monoxide formed, more hydrogen peroxide than would have been expected, and relatively little formaldehyde. Very dilute mixtures of ethylene and ozone were found to react rapidly and almost completely when well mixed. If no moisture is present, the ozonide decomposes into formic acid and formaldehyde or their decomposition products. In presence of water, more or less hydrolysis to formaldehyde and hydrogen peroxide occurs. If the ozone present is not sufficiently dilute, as compared with the ethylene, some oxidation of formaldehyde to formic acid takes place. Most of the hydrogen peroxide formed decomposes, but some may react with ozone or may oxidise formaldehyde. The rate of decomposition of the ozonide appears to be proportional to the concentration in which it is formed. The presence of ammonia during the reaction appears to increase the yield, probably by combining with the formaldehyde as it is formed, giving hexamethylenetetramine; no nitrate or nitrite was detected.

E. H. R.

**The Condensation Products of Methyl Ethyl Ketone.** JOHN E. ECKLEY and W. WARREN HOWE (*J. Amer. Chem. Soc.*, 1923, 45, 1917—1925).—The action of hydrogen chloride on cold methyl ethyl ketone gives  $\gamma$ -methyl- $\Delta^7$ -hepten- $\alpha$ -one, b. p. 156—160°/625 mm.,  $d_4^{20}$  0.8628,  $n_D^{20}$  1.4453 (cf. Bodroux and Tabary, A., 1909, 766); the constitution of this is proved by the production of propionic acid when it is oxidised by means of cold dilute potassium permanganate solution (cf. Becker and Thorpe, T., 1922, 121, 103). It gives a liquid oxime, b. p. 132—137°/17 mm., and a semicarbazide-semicarbazone, microscopic prisms, m. p. 265—266° (decomp.). The semicarbazone, m. p. 114—115°, prepared by Bodroux and Tabary (*loc. cit.*) is a mixture. A second product of the above reaction is homophorone,  $C_{12}H_{20}O$ , a clear, slightly yellow-coloured liquid with a camphor-like odour and taste, b. p.

206–210°/625 mm.,  $d_4^{20}$  0.8857,  $n_D^{20}$  1.4792. When the condensation is effected by means of cold concentrated sulphuric acid, or of sodium ethoxide, there are formed, in addition to the above products, two ketones homologous with isophorone: (1) a clear, yellow liquid having a faint odour and taste of terpene, b. p. 256–260°/630 mm.,  $d_4^{20}$  0.9492,  $n_D^{20}$  1.5045; (2) a golden-brown, somewhat viscous liquid, having a camphor-like odour and taste, b. p. 280–285°/630 mm.,  $d_4^{20}$  0.9693,  $n_D^{20}$  1.5115. The same two compounds are formed when  $\gamma$ -methyl- $\Delta^7$ -hepten- $\epsilon$ -one is condensed with methyl acetate by means of alcoholic sodium ethoxide solution. Hence one of these ketones, although it is not known which, is 1:2:3:4-tetramethyl-4-ethyl- $\Delta^1$ -cyclohexen-6-one, the other being 1:2-di-methyl-1:5-diethyl- $\Delta^4$ -cyclohexen-3-one. W. S. N.

**Bromination of Compounds containing the Carbonyl Group.** (a) Pyruvic Acid. (b) Acetophenone. CHARLES FREDERICK WARD (T., 1923, 123, 2207–2213).

**Catalytic Hydrogenation and Steric Hindrance.** Nonanones. G. VAVON and D. IVANOV (*Compt. rend.*, 1923, 177, 453–456).—Hydrogenation of four isomeric ketones of the formula  $C_9H_{18}O$  (nonan- $\epsilon$ -one,  $\gamma$ -methyloctan- $\delta$ -one,  $\gamma\epsilon$ -dimethylheptan- $\delta$ -one, and tetramethylpentan- $\gamma$ -one) to the corresponding alcohols in presence of platinum black shows that the extent of the reduction follows the law of steric hindrance. A similar effect, but to a lesser extent, was observed in the formation of oximes and phenylhydrazones. The following compounds are described: nonan- $\epsilon$ -ol (dibutylcarbinol), b. p. 194°,  $d_4^{18}$  0.823,  $n_D^{18}$  1.4289;  $\gamma$ -methyloctan- $\delta$ -ol, b. p. 180°,  $d_4^{18}$  0.834,  $n_D^{18}$  1.4325;  $\gamma\epsilon$ -dimethylheptan- $\delta$ -ol, b. p. 171°,  $d_4^{18}$  0.836,  $n_D^{18}$  1.4330. The corresponding allophanates melt at 158°, 160°, and 163° respectively. H. J. E.

**The Methylation of Sugars.** MARC BRIDEL (*Bull. Soc. chim.*, 1923, [iv], 33, 1005–1058).—A lecture delivered at the Collège de France on 17 March, 1923.

**The Effect of Trichloroacetic Acid in Preventing Reduction by Reducing Sugars.** B. M. MARGOSCHES and FRITZ STEINDLER (*Naturprodukte*, 1923, 67–72).—Chloroform is known to reduce Fehling's solution. It is therefore surprising to find that trichloroacetic acid not only does not reduce Fehling's solution but hinders its reduction by chloroform and formaldehyde. Further, it is found that comparatively small quantities of trichloroacetic acid retard the reduction of Fehling's solution by arabinose, dextrose, galactose, laevulose, maltose, and lactose, and larger quantities prevent reduction altogether. There appears to be a numerical relationship between the minimum quantities of trichloroacetic acid required to prevent reduction with different sugars, but the significance of this relationship is not clear. E. H. R.

**Hemicellulose. III. Decomposition of Lichenin by Ferments.** HANS PRINGSHEIM and KARL SEIFERT (*Z. physiol. Chem.*, 1923, 128, 284–289).—Lichenin, a polysaccharide obtained from

Island moss, *Cetraria islandica*, is fermented by the enzymes of malt yielding dextrose (isolated as glucosazone). This reaction has an optimum at  $P_H$  5. Lichenin is hydrolysed also by acid but less rapidly than starch.

W. O. K.

**Structural Units of Starch determined by X-Ray Crystal Structure Method.** O. L. SPONSLER (*J. Gen. Physiol.*, 1923, 5, 757—776).—Starch when submitted to X-ray analysis gives lines which are less intense and more diffuse than those produced, e.g. by sodium chloride, but nevertheless can be measured. Their position is satisfactorily explained on the supposition that there is in starch a lattice of the tetragonal system, the elementary cell of which is a square prism with dimensions  $5.94 \times 5.94 \times 5.05$  Å. The volume of this cell corresponds with that of the unit group,  $C_6H_{10}O_5$ . A structure built up of concentric layers of such units would give reflections the intensity of which would be in general agreement with the experimental results.

W. O. K.

**Determination of the Viscosity of Cellulose** (*Research Dept. Woolwich, Rept. No. 22, Part III*).—Most forms of cellulose have been found to be irregular in viscosity throughout their mass, when dissolved in cuprammonium solutions so that sampling must be on a large scale. To ensure the formation of clear solutions of uniform viscosity, thorough disintegration and teasing of the cellulose sample is essential. Drying at elevated temperatures or treatment of the cellulose with boiling water or dilute alkali solutions affects the viscosity and is inadmissible. Joyner's method for the preparation of cuprammonium solutions (*T.*, 1922, 121, 1511, 2395) is satisfactory and to be recommended. An apparatus for preparing such solutions is described and also a method of filling viscosimeter tubes. The original specifications for the cuprammonium solvent have been found to be too wide; to obtain consistent results the narrower specifications outlined in the report must be adopted.

T. S. W.

**Qualitative and Quantitative Differences between some Wood and Straw Lignins.** ERNST BECKMANN, OTTO LIESCHE, and FRITZ LEHMANN [with K. F. LINDNER] (*Biochem. Z.*, 1923, 139, 491—508).—A detailed investigation of the nature of wood and straw lignins isolated by alkali treatment at different temperatures. The straws investigated were those of rye, barley, oats, and rice, and the woods, maple, red beech, fir, and spruce. In each case the straw or wood was dried in air, ground to a meal, and after removal of the resins, fats, and waxes by exhaustive ethereal extraction, equal quantities of each meal were subjected to the action of 1.5% sodium hydroxide in a series of consecutive extractions as follows: (a) Forty-eight hours at room temperature, (b) six hours' boiling in a reflux apparatus, (c) six hours in an autoclave at 3 atm., (d) six hours at 6 atm., (e) six hours at 9 atm. Methods (d) and (e) were required only in the cases of the woods. The completion of the extraction was indicated by the destruction of the fibrous structure and the absence of red coloration with phloroglucinol hydrochloride. The

lignins extracted in each method were isolated by Beckmann's process (A., 1921, i, 546), and methoxyl estimations were made on each sample. In successive extraction methods, the straws gave diminishing yields of lignins, which became increasingly darker and less soluble in pyridine, acetic acid, or alcohol as the temperature of extraction rose. The methoxyl content was at a maximum in those isolated by method (b). The woods yielded increasing amounts of lignins in successive extractions up to method (d), at which the methoxyl content was also, in general, at a maximum. The two pine woods gave markedly uniform results, but more variation was encountered in the deciduous woods, and the latter contained less lignin of a higher methoxyl figure than did the former. As in the case of the straw lignins, increasing temperature of extraction gave products of a darker colour and of more restricted solubilities in basic, acid, or neutral solvents. In all cases the total lignin extracted was less than that estimated to be present in the original material by Willstätter's method, the difference being accounted for by experimental losses and the presence of silica in the straws (more especially in rice straw). A series of experiments on maple wood meal was carried out in which each method of extraction was continued until no further lignin was obtained before the next method in the series was employed. Methods (c), (d), and (e) were capable of removing all the extractable lignin but this was still found to be less than the total in the original material. Parallel extractions of maple wood meal with 1.5% and 3.0% sodium hydroxide showed that the more concentrated alkali gave higher yields of lignin, but the appearance and methoxyl content of corresponding fractions were the same. The lignins of winter rye straw at different periods of growth were investigated by these methods. The lignin content and methoxyl figure increases with the age of the plant, the increases being more marked in the earlier stages of growth. The results are given of various elementary analyses of the lignins isolated as above described, and in a chemical examination of their decomposition products the presence of protocatechuic acid, pyrocatechol, and pyrogallol was revealed. As a result of demethylation of a rye lignin by hydriodic acid, a dark brown, resinous substance was obtained to which the empirical formula  $C_{36}H_{33}O_6I$  is provisionally ascribed. Maple and pine wood lignins on demethylation gave similar but more complex substances of empirical formulae respectively,  $C_{72}H_{45}O_{12}I$  and  $C_{108}H_{88}O_{18}I$ . No definite conclusion is drawn from the results of various experiments designed to elucidate the phloroglucinol reaction of native lignin. J. P.

**Lignin Prepared by the Hydrochloric Acid Process.** ERIK HAGGLUND (*Naturprodukte*, 1923, 24—35, and *Cellulosechem.*, 1923, 4, 73—77).—Lignin prepared by Willstätter's process, by treating pine wood with highly concentrated (45%) hydrochloric acid, evolves furfuraldehyde when subsequently distilled with hydrochloric acid. Experiments now described indicate that the carbohydrate from which the furfuraldehyde is derived forms an integral

part of the lignin molecule. The carbohydrate can be removed by hydrolysing the lignin with hot 5% sulphuric acid or by the prolonged action of cold 45% hydrochloric acid. It was identified by its optical rotatory power and by its osazone as arabinose, and is present in pine wood lignin to the extent of 4.5%. Pyrocatechol and formic acid were found among the fusion products of lignin with alkali hydroxide. The methoxyl content of lignin is 14.68%, rising to 15.2% after complete removal of carbohydrate. E. H. R.

**Characteristics of the Two Crystalline Forms of Glycine.** C. A. BRAUTLECHT and N. F. EBERMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1934—1941).—The action of hydrogen chloride, of bromine vapour, or of sulphur dioxide, with or without moisture, shows that moisture rapidly effects an equilibrium between the plate and needle forms of glycine, and that any difference in these forms will only appear if water is completely excluded. The dry crystals do not differ chemically or in m. p. when dried at 103° and ground to pass a 0.3 mm.-mesh sieve, or when air-dried and ground. Bromine does not form a compound with glycine, varying amounts being taken up temporarily, according to the amount of moisture present and time of contact, and lost again on exposure to the air. Neither phosphorus trichloride nor phosphorus pentachloride acts on glycine in carbon disulphide solution. In the formation of glyceryl chloride by the action of acetyl chloride and phosphorus pentachloride (Fischer, A., 1905, i, 863), it is evidently the acetyl chloride which leads to the formation of glyceryl chloride. Other compounds, some of which contain phosphorus, are also produced in this reaction. W. S. N.

**Preparation of Homologues of Anilinolactic Acid.** ÉTABLISSEMENTS POULENC FRÈRES (Fr. Pat. 532465; from *Chem. Zentr.*, 1923, ii, 1062).—Aniline or its homologues are allowed to react with halogenohydroxycarboxylic acids of the composition  $\text{CH}_2\text{X}\cdot\text{CR}(\text{OH})\cdot\text{CO}_2\text{H}$  or  $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CHX}\cdot\text{CO}_2\text{H}$ , where R = alkyl or aryl. The amino-acids are converted by usual methods into ethers or salts. By the action of aniline on  $\beta$ -chloro- $\alpha$ -hydroxy- $\alpha$ -methylpropionic acid,  $\beta$ -anilino- $\alpha$ -hydroxy- $\alpha$ -methylpropionic acid,  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$ , is obtained; it forms crystals, m. p. 60°.  $\beta$ -p-Éthoxyanilino- $\alpha$ -hydroxy- $\alpha$ -methylpropionic acid,  $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$ , from *p*-phenetidine, has m. p. 180—181°.  $\alpha$ -Bromo- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid with aniline yields anilinophenyl-lactic acid,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{H}$ , m. p. 144°. G. W. R.

**Alkyl Derivatives of Dicyanodiamide and of Dicyanodiamidine.** G. PELLIZZARI (*Gazzetta*, 1923, 53, i, 384—392; cf. A., 1919, i, 134; 1921, i, 363, 403, 620).—The action of nitrous acid on phenylmethyldiguanide and on piperidyldiguanide yields the corresponding substituted dicyanodiamides, the non-substituted guanidyl group being transformed into the cyano-amino-residue. In either case, however, a second compound is formed owing to

$n n^*$

the conversion of the substituted guanidyl group into the carbamide group;  $\text{NR}_2\text{C}(\text{NH})\cdot\text{NH}\cdot \rightarrow \text{NR}_2\text{CO}\cdot\text{NH}\cdot$ . Thus, phenylmethyldiguanide gives cyanophenylmethylguanidine, which is neutral and has characteristics similar to those of dicyanodiamide, and guanylmethylcarbamide, which is a substituted dicyanodiamidine. Under similar conditions, piperidyldiguanide yields cyanopiperidyldiguanidine and guanylcarmylpiperidine.

Only a single product, cyanophenyleneguanidine, is obtained by the action of nitrous acid on *o*-phenylenediguanide, since the latter is substituted at two different nitrogen atoms and transformation of the guanidyl into the carbamide group is not possible; *o*-phenyleneguanidine, with which this possibility exists, is converted into phenylenecarbamide by nitrous acid. Phenyldiguanide, when treated with nitrous acid, yields only guanylmethylcarbamide, without the corresponding dicyanodiamide.

The two substituted dicyanodiamides obtained resemble their parent compound in behaviour. When they are gently boiled with dilute acid, the cyanogen group undergoes hydration to the carbamide group with formation of the corresponding guanylcarmamides, which have the substituent groups in the guanidyl residue, and are thus isomeric with the compounds obtained by means of nitrous acid. Thus, cyanophenylmethylguanidine,



gives phenylmethylguanylcarmamide,  $\text{NMePh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , which is isomeric with guanylmethylcarbamide,



and 1-cyanoguanidyldipiperidine,  $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN}$ , gives 1-carbamylguanyldipiperidine,  $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , isomeric with 1-guanylcarmaldipiperidine,  $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ . With nickel salts these dicyanodiamidines yield amorphous precipitates and not characteristic compounds such as that given by dicyanodiamidine.

*Cyanophenylmethylguanidine* crystallises in transparent, colourless laminae or slender needles, m. p.  $143^\circ$ , is neutral towards litmus, and forms a *hydrochloride* decomposing at about  $165^\circ$ .

*Guanylmethylcarbamide* forms isolated white, prismatic crystals or spherical aggregates, m. p.  $175^\circ$ , and gives an aqueous solution alkaline to litmus. Its *nitrate*,  $\text{C}_6\text{H}_{12}\text{ON}_4\cdot\text{HNO}_3$ , crystallises in long, transparent needles and decomposes at about  $190^\circ$ .

*Phenylmethylguanylcarmamide* separates in white needles, m. p.  $141^\circ$ , and at  $160\text{--}170^\circ$  yields gas and a solid compound, which is probably a substituted biuret. In aqueous solution it is alkaline to litmus, and with copper sulphate and ammonia it forms a characteristic peach-blossom-coloured compound, whilst its isomeride gives a pale blue, flocculent precipitate under similar conditions.

1-Cyanoguanidinopiperidine,  $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 & \text{CH}_2 \\ \text{CH}_2 & \text{CH}_2 \end{smallmatrix}\rangle\text{N}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN}$ , forms lustrous lamellae, m. p.  $172\text{--}173^\circ$ , resembling those of dicyanodiamide, and is neutral towards litmus.

1-Guanylcarmaldipiperidine forms transparent, prismatic crystals or white masses of slender needles, m. p.  $177\text{--}178^\circ$ , and turns red

litmus paper blue. The *picrate*,  $C_7H_{11}ON_4C_6H_3O_7N_3$ , crystallises in lustrous, yellow lamellæ, m. p. about  $190^\circ$  (decomp. and separation of a solid).

1-Carbamylguanylpiperidine is obtained as a syrup and yields a *picrate*,  $C_7H_{11}ON_4C_6H_3O_7N_3$ , which forms lustrous, yellow needles, m. p.  $245^\circ$  with previous softening.

Guanylphenylcarbamide,  $NHPh \cdot CO \cdot NH \cdot C(NH) \cdot NH_2$ , forms long, transparent, colourless crystals, m. p.  $143-144^\circ$ , yields an alkaline aqueous solution, and with copper sulphate and ammonia gives a brilliant green, pulverulent precipitate. Its *nitrate* ( $+HNO_3$ ) separates in lustrous, colourless crystals and decomposes at  $211-213^\circ$ , and its *picrate* ( $+C_6H_3O_7N_3$ ) forms slender, yellow needles and begins to decompose at about  $230^\circ$ . The constitution of guanylphenylcarbamide is established by the fact that it yields aniline and guanidine and only traces of ammonia when hydrolysed by means of dilute nitric acid; the isomeric phenylguanylicarbamide has m. p.  $62-63^\circ$  (cf. Walther and Grieshammer, A., 1916, i, 173).

T. H. P.

The Isomorphism of the Amides and Substituted Amides of Dichloro- and Chlorobromo-acetic Acids. PHYLLIS V. MCKIE (T., 1923, 123, 2213-2217).

The Hydrates of Potassium and Lithium Platinocyanides and the System Potassium Platinocyanide-Lithium Platinocyanide-Water. HENRY TERREY and VICTOR GEORGE JOLLY (T., 1923, 123, 2217-2222).

The Action of the Grignard Reagent on Nitriles. Glutaronitrile. P. BRUYLANTS (Bull. Soc. chim. Belg., 1923, 32, 307-310).—The reaction between two molecular proportions of magnesium phenyl bromide and one of glutaronitrile leads to the formation of the hydrobromide of  $\gamma$ -benzyliminobutyronitrile, m. p.  $174^\circ$ , which gives a chloroplatinate, m. p.  $197^\circ$  (decomp.), and a *picrate*, m. p.  $200-202^\circ$ . The hydrobromide of the base may be crystallised from warm water, and its aqueous solution, when treated with semicarbazide acetate, gives a precipitate of the semicarbazone of  $\gamma$ -benzoylbutyronitrile, m. p.  $94-95^\circ$ .  $\gamma$ -Benzyliminobutyronitrile, m. p.  $88-90^\circ$ , is obtained by the action of dry ammonia gas on a suspension of its hydrobromide in anhydrous ether. In aqueous solution, the action of ammonia on the hydrobromide is to give  $\gamma$ -benzoylbutyronitrile, m. p.  $158-159^\circ$ , which can be hydrolysed to the corresponding  $\gamma$ -benzoylbutyric acid of known constitution.

H. H.

Reactions of certain Aromatic Derivatives. A. ANGELI (Atti R. Accad. Lincei, 1923, [v], 32, i, 443-449).—The author quotes and co-ordinates further data which confirm the rule that two substituents, occupying ortho- or para-positions in an aromatic ring, behave in many reactions as though they were directly united one to the other (A., 1920, i, 665). Moreover, this rule, which holds with systems composed either of a single aromatic ring or of two aromatic rings joined by characteristic unsaturated chains,

appears to be applicable to certain derivatives of quinoline and, in all probability, to pyridine also.

T. H. P.

**The Solubility of Liquid Hydrocarbons in Superheated Water.** A. JAEGER (*Brennstoff-Chem.*, 1923, 4, 259—260).—The apparatus described by Fischer (*ibid.*, 225) was used to determine the solubilities in water at temperatures from 100° to 300° of (a) benzene, (b) toluene, (c) xylene, (d) tetrahydronaphthalene, and various mixtures of hydrocarbons. The solubilities of the aromatic hydrocarbons are greater than those of the aliphatic; the higher the boiling point of a hydrocarbon the less is its solubility. The following results expressed in c.c. of hydrocarbon dissolved in 100 c.c. of water were obtained: at 100°, (a) 0.2; (b) <0.1; (c) trace; (d) trace; at 150°, (a) 0.6, (b) 0.2; (c) 0.1; (d) 0.02; at 200°, (a) 2.1; (b) 0.7; (c) 0.35; (d) 0.04; at 250°, (a) 7.3; (b) 2.8; (c) 1.1; (d) 0.4; at 285° (a) 10.6; at 300°, (a) 14.6; (b) 13.0. The various solubilities increase very rapidly with temperature excepting benzene above 250°; that hydrocarbon is then near its critical temperature.

T. S. W.

**Chemical Composition of Lignite Tar.** J. K. PFAFF and A. KREUTZER (*Z. angew. Chem.*, 1923, 36, 437—439).—A toluene fraction (b. p. 111.5—112.5°; S=4.4%), obtained from lignite tar, contained about 3% of  $\alpha$ -thiotolene, which was identified by conversion into  $\alpha$ -methyl- $\alpha$ -acetothienone. The ketone content of lignite tar oils, which was found to vary from 2.2—4.5%, was determined by warming the oil with excess of phenylhydrazine and estimating the unchanged base by oxidation with boiling Fehling's solution [cf. *J.S.C.I.*, 1923, 967A].

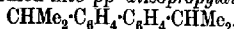
W. T. K. B.

**Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. III. The Reduction of Nitrobenzene by Sodium in Liquid Ammonia.** GEORGE F. WHITE and KENNETH H. KNIGHT (*J. Amer. Chem. Soc.*, 1923, 45, 1780—1787).—Nitrobenzene and nitrosobenzene are reduced by means of sodium in liquid ammonia solution to the disodium derivative of phenylhydroxylamine (cf. Schmidt, A., 1900, i, 20), which probably has the structure  $\text{NPhNa}\cdot\text{ONa}$ . It is reconverted into nitrobenzene if air is passed into its solution in liquid ammonia, but the free base may be liberated by the action of ammonium chloride. By further reduction of this disodium derivative in liquid ammonia solution, disodioaniline is formed, from which aniline is liberated by the action of ammonium chloride or water. Phenylhydroxylamine itself is reduced directly to aniline in liquid ammonia solution. Azoxybenzene and azobenzene are not formed by direct reduction of nitrobenzene in liquid ammonia, but if the partly reduced mixture is poured into water, they are produced as secondary reaction products of phenylhydroxylamine in the alkaline, aqueous solution. Azoxybenzene is reduced to azobenzene, which is further reduced to a disodium derivative of hydrazobenzene. This gives hydrazobenzene when treated with ammonium

chloride, and is further reduced by sodium in ammonia solution to disodium anilide, whilst hydrazobenzene itself is reduced to monosodium anilide. Mono- and di-alkylanilines are formed in liquid ammonia solution by the action of alkyl halides on mono- and di-sodium anilides, respectively.

W. S. N.

**Preparation of the Magnesium Compound of *p*-Bromocumene and its Application to Organic Syntheses.** L. BERT (*Compt. rend.*, 1923, 177, 452—453).—Details of the action of magnesium on *p*-bromocumene are given; the resulting substance is stated to be as easy to prepare as the corresponding *p*-bromobenzene derivative. In the reaction, about 15% of the *p*-bromocumene was transformed into *pp'*-diisopropylidiphenyl,



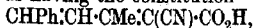
brilliant, colourless plates, m. p. 64—65°. Various syntheses have been effected by means of the magnesium compound. H. J. E.

**Chlorosulphonyl Derivatives of Aromatic Amines.** ROWLAND NICHOLAS JOHNSON and SAMUEL SMILES (*T.*, 1923, 123, 2384—2388).

**Preparation of Intermediate Compounds [*m*-Chloro-, *m*-Bromo-, and *m*-Iodo-phenol] for the Production of Colouring Matters.** BRITISH DYESTUFFS CORPORATION, LTD., and HERBERT HENRY HODGSON (*Brit. Pat.* 200714).—A substantially quantitative yield of *m*-chlorophenol is obtained by diazotising *m*-chloroaniline and decomposing the diazo-solution, care being taken that the latter is free from nitrous acid and that the *m*-chlorophenol is removed from the reaction liquid by distillation in steam with such rapidity that combination cannot take place with further quantities of diazo-compounds. Diazotisation is effected in dilute sulphuric acid, addition of the nitrite solution to the paste of *m*-chloroaniline sulphate being stopped before all the crystals of the latter have disappeared. The filtered diazo-solution is dropped into boiling dilute sulphuric acid, through which a current of steam is blown. The liquid is simultaneously heated so as to maintain substantially the same volume. *m*-Bromo- and *m*-iodo-phenol are obtained in the same way from *m*-bromo- and *m*-iodo-aniline, respectively.

W. T. K. B.

**The Reaction between Cyanoacetic Esters and Styryl Methyl Ketone.** E. P. KOHLER and PAUL ALLEN, jun. (*J. Amer. Chem. Soc.*, 1923, 45, 1987—1990).—The compound described by Haworth (*T.*, 1909, 95, 480) as having the constitution



m. p. 188°, is identical with cyanophenyldihydroresorcinol, m. p. 180° (Vorländer, A., 1897, i, 272), the constitution of which is confirmed by oxidising it to phenylsuccinic acid by means of cold alkaline potassium permanganate solution. The acid amide, and the monobasic acid, m. p. 190° (m. p. 187—188° according to Vorländer, *loc. cit.*), described by Haworth, must also be regarded as dihydroresorcinol derivatives. The primary product in the

formation of cyanophenylhydrosorcinol from methyl cyanoacetate and styryl methyl ketone is *methyl α-cyano-γ-acetyl-β-phenylbutyrate*, a very pale yellow liquid, b. p. about 186°/2 mm. (semi-carbazone, minute, white needles, m. p. 156—157°). Or, if ethyl cyanoacetate is used, *ethyl α-cyano-γ-acetyl-β-phenylbutyrate*, a very viscous oil, b. p. 203°/12 mm. These can only be isolated if the condensation between the cyano-ester and the unsaturated ketone is conducted in the presence of a small quantity of sodium methoxide or ethoxide, since this causes ring formation with elimination of methyl or ethyl alcohol. *Methyl β-phenyl-γ-acetylmalonate*,  $\text{COMe}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$ , a colourless solid, m. p. 64°, is formed by keeping a methyl-alcoholic solution of the above methyl cyano-ester after saturating with hydrogen chloride, or by the direct addition of methyl malonate to styryl methyl ketone in the presence of cold sodium methoxide.

W. S. N.

**Manufacture of Thymol.** HOWARDS & SONS, LTD., and JOHN WILLIAM BLADGEN (Brit. Pat. 200151).—*m*-Cresol is condensed with isopropyl alcohol in the presence of phosphoric acid at a temperature of 70—80°. If the reaction temperature is higher (e.g., 150°), a condensation product melting at 114° and possessing antiseptic properties is obtained.

W. T. K. B.

**The Humic Acid Problem.** WALTER FUCHS (*Naturprodukte*, 1923, 98—107).—The author discusses current opinions on the constitution of humic acid, and compares experimentally the properties of the humic acid prepared from resorcinol by Stamberger (following abstract) with those of commercial humic acid from peat. The latter can be methylated in alkaline solution without being thrown out of solution; it must therefore contain both phenolic and carboxyl groups. By fusion with potassium hydroxide, it gives a product having acid properties and giving a chocolate coloration with ferric chloride. With ammonia, the humic acid forms a compound from which only part of the nitrogen can be removed by distillation with alkali. It is suggested that oxygen of a furan ring is displaced by nitrogen with formation of a pyrrole ring. The nitrogen-containing product is more resistant to oxidation than the original humic acid, and it reacts with nitrous acid as though it contained an imide group. It is concluded that humic acid contains both phenol and furan nuclei. The formation of such a complex compound from a variety of natural products is conceivable.

E. H. R.

**Synthetic Humic Acids.** PAUL STAMBERGER (*Naturprodukte*, 1923, 108—112).—A synthetic humic acid is obtained when resorcinol is heated with sublimed ferric chloride in aniline or quinine solution. The product is qualitatively similar to that obtained by Eller and Koch by oxidation of phenols capable of forming quinones (A., 1920, i, 733). It contains no nitrogen, but reacts with aqueous ammonia to form a "*N*-humic acid" containing 6.36% N. The humic acid can be methylated with methyl sulphate and benzoylated with benzoyl chloride. When fused with potassium

hydroxide, it gives an indistinctly crystalline product giving a chocolate coloration with ferric chloride, the coloration being intensified by hydrogen peroxide. The fusion product gives a benzoyl derivative, m. p. 100–101°, and a bromo-derivative, m. p. 120°. Humic acids prepared from starch is qualitatively similar to the above, but requires heating in ammonia gas at 110–120° to give a "humic acid". E. H. R.

**Derivatives of ortho-Thiolphenols.** DAVID TEMPLETON GIBSON and SAMUEL SMILES (F., 1923, 123, 2388–2393).

**Preparation of Urethanes of Secondary Aliphatic-aromatic Alcohols.** ÉTABLISSEMENTS POULENC FRÈRES (Fr. Pat. 532464; from *Chem. Zentr.*, 1923, ii, 1062).—Carbonyl chloride is allowed to react with phenylethylcarbinol,  $\text{CH}_2\text{Ph}\cdot\text{OH}$ , or its homologues in the presence or absence of tertiary bases such as trimethylamine or dimethylaniline, and the chloroformates thereby obtained are treated with ammonia. The alcohols used are obtained by the action of magnesium alkyl halides on benzaldehyde. For example, phenylethylcarbinol obtained by the action of magnesium ethyl bromide on benzaldehyde is allowed to react with carbonyl chloride in benzene solution at 10° with addition of trimethylamine or dimethylaniline. After addition of ice, the benzene solution is dried and saturated with ammonia. After removal of ammonium chloride and dimethylaniline, phenylethylcarbinol urethane,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$ , is obtained; it has m. p. 89°. Phenylpropylcarbinol urethane has m. p. 80°; it is prepared from phenylpropylcarbinol, b. p. 119°/12 mm. Phenylbutylcarbinol, b. p. 132°/14 mm., yields a urethane having m. p. 75°. G. W. R.

**Spontaneous Dissociation of Triphenylmethyl Disulphide with the Formation of Triphenylmethyl.** The Potassium Derivative of Triphenylcarbinol and its Use as a Synthetic Agent. F. F. BLICKE (*J. Amer. Chem. Soc.*, 1923, 45, 1965–1969).—Triphenylmethyl disulphide dissociates spontaneously in benzene solution at the ordinary temperature with formation of triphenylmethyl, which is isolated as its peroxide (cf. this vol., i, 364). The potassium derivative of triphenylmethyl alcohol is prepared by the action of the alcohol on metallic potassium in boiling xylene solution. It forms colourless, transparent crystals containing approximately 1 mol. of xylene of crystallisation. It reacts in boiling benzene solution with methyl iodide, giving triphenylmethyl methyl ether, with ethyl iodide giving ethylene, triphenylmethyl alcohol, and potassium iodide, and with benzoyl chloride giving triphenylmethyl benzoate. The potassium compound reacts with triphenylmethyl sulphur chloride in cold benzene solution, with evolution of heat, to give a clear, reddish-brown solution from which triphenylcarbinol and triphenylmethyl peroxide are isolated. It is likely that triphenylmethyl thioperoxide is produced initially; the peroxide may be formed by interaction between the thioperoxide and unchanged potassium compound:

$$2\text{Ph}_3\text{C}\cdot\text{S}\cdot\text{O}\cdot\text{CPh}_3 + 4\text{Ph}_3\text{C}\cdot\text{OK} = 3\text{Ph}_3\text{C}\cdot\text{O}\cdot\text{O}\cdot\text{CPh}_3 + \text{Ph}_3\text{C}\cdot\text{CPh}_3 + 2\text{K}_2\text{S}.$$

This explanation is supported by the observation of Vorländer and Mittag (A., 1913, i, 1335) that triphenylmethyl sulphur chloride reacts with sodium methoxide to give triphenylmethyl methyl thioperoxide. The opinion of those authors that the product of this reaction, when excess of sodium methoxide is used, is triphenylmethyl peroxide, has now been definitely proved to be correct. The potassium derivative of triphenylmethyl alcohol reacts with triphenylmethyl chloride in cold benzene solution, but does not give triphenylmethyl ether; the only product isolated is *p*-hydroxy-triphenylmethyl alcohol, which is probably present as its anhydride, diphenylquinomethane. The potassium compound reacts immediately with iodine, phosphorus trichloride, or other substances containing reactive halogen.

W. S. N.

**A Study of the Phytosterols of Corn [Maize] Oil, Cottonseed Oil, and Linseed Oil.** R. J. ANDERSON and M. G. MOORE (J. Amer. Chem. Soc., 1923, 45, 1944—1953).—Maize oil contains a relatively high percentage of unhydrolysable matter, as estimated by a modification of Bömer's method (Z. Nahr. Genussm., 1898, 1, 21), amounting in the crude oil to 2.01%, and in the refined edible oil to 1.68%. This unsaponifiable matter consists largely of phytosterol, which is identical with sitosterol. It has m. p. 137.5°,  $[\alpha]_D^{25}$  -34.38°; its acetate has m. p. 127°. It does not contain any stigmasterol. These results are in agreement with those of Gill and Tufts (A., 1903, i, 417).

The observations of Wagner and Clement (Z. Nahr. Genussm., 1909, 17, 266) on cotton-seed oil are confirmed. It contains at least two phytosterols, which have, respectively, m. p. 138—139° and 134—135°,  $[\alpha]_D^{25}$  -34.19° and -33.61°, the acetates having m. p. 124° and 119°, respectively. The separation of these two fractions by crystallisation is very difficult, and it is not thought that either of them is homogeneous.

Two phytosterols have been isolated from linseed oil, having, respectively, m. p. 138° and 134° (indefinite),  $[\alpha]_D^{25}$  -34.22° and -31.16°, acetates, m. p. 129—130° and 124° (cf. Bömer and Winter, Z. Nahr. Genussm., 1901, 4, 865).

None of the phytosterols isolated contains as much as 1 mol. of water of crystallisation, the irregular loss observed on drying corresponding roughly with 0.5 molecule.

W. S. N.

**Japanese Birdlime. III.** HIDEKICHI YANAGISAWA and NORIKAZU TAKASHIMA (J. Pharm. Soc. Japan, 1923, No. 494, 251—258; cf. A., 1921, i, 760; 1922, i, 652).—Trochol,  $C_{26}H_{42}O_2$ , isolated from the saponification product of Japanese birdlime, *Trochodendron aralioides*, yields a diphenylcarbamate,  $C_{26}H_{42}O_2(CO-NHPh)_2$ , colourless prisms, m. p. 167°; formate, nacreous scales, m. p. 306°, and phthalate, a white, crystalline powder, m. p. 224—228°. On oxidation with hydrogen peroxide in glacial acetic acid, the alcohol gave a dihydroxymonoketone, trocholonone,  $C_{26}H_{42}O_3$ , an amorphous powder, m. p. about 100°, trochol peroxide,  $(C_{26}H_{42}O_2)_2$ , colourless scales, m. p. 215°; semicarbazone, fine, white needles, m. p. 290°; acetyl derivative, fine, white needles, m. p. 205°; oxime,

small, white needles, m. p.  $217^{\circ}$ , and *trocholic acid*,  $C_{26}H_{42}O_4$ , white granules, m. p.  $282^{\circ}$  (*diacetate*, white, crystalline powder, m. p.  $145^{\circ}$ ). The authors conclude that trochol is a secondary-tertiary, but not a primary alcohol. When a mixture of trochol and chromic anhydride is treated with water, an odour of butyric acid is produced, and acetic acid can be isolated by the distillation of the mixture with steam.

K. K.

**Esterification. I. Esterification of the cycloParaffin-mono-carboxylic Acids.** G. D. ADVANT and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1923, 6, 41—68; cf. T., 1912, 101, 237).—The investigation deals with the influence of ring-formation on rates of esterification (cf. Menschutkin, T., 1906, 89, 1532). The esterifications were carried out in absolute ethyl alcohol at  $25^{\circ}$ . The modified formula of Goldschmidt and Udby (A., 1907, ii, 852) for unimolecular reactions was found to give fairly good constants. The values of the constant,  $K$ , obtained were as follows (the figures in brackets are the corresponding dissociation constants  $\times 10^3$ ): *cyclo*Butanecarboxylic acid, 0.544 (1.82). *cyclo*Pentanecarboxylic acid, 0.196. *iso*Butyric acid, 0.156 (1.62). *cyclo*Hexanecarboxylic acid, 0.0812 (1.26).  $\alpha$ -Methyl-*n*-butyric acid, 0.0384 (1.68). *cyclo*Propanecarboxylic acid, 0.0324 (1.44).  $\alpha$ -Ethyl-*n*-butyric acid, 0.00313 (2.02).  $\alpha$ -Ethyl-*n*-valeric acid, 0.00311. Goldschmidt and Udby's results were confirmed in that the values of  $K$  vary somewhat with the concentration of the catalyst. In the cases of the disubstituted acetic acids examined, *isobutyric* acid is most readily esterified,  $\alpha$ -ethyl-*n*-butyric and  $\alpha$ -ethyl-*n*-valeric acids least readily. The methyl group has the least inhibiting effect, whilst the ethyl and *n*-propyl groups have practically the same effect. By comparing the aliphatic and the corresponding cyclic acids, the following ratios for  $K$  are obtained: *isobutyric* acid: *cyclo*propanecarboxylic acid = 0.25:1;  $\alpha$ -methyl-*n*-butyric acid: *cyclo*butanecarboxylic acid = 13.0:1;  $\alpha$ -ethyl-*n*-butyric acid: *cyclo*pentanecarboxylic acid = 80.0:1;  $\alpha$ -ethyl-*n*-valeric acid: *cyclo*hexanecarboxylic acid = 28.0:1. This agrees with Menschutkin's acetylation results (*loc. cit.*), in that the maximum occurs in the pentamethylene series. In the case of the cyclic acids alone, the ratios for  $K$  are: 3-ring = 1; 4-ring = 16; 5-ring = 7; 6-ring = 3. It is possible that the low values for the *cyclo*propanecarboxylic acid may be due to tautomeric change.

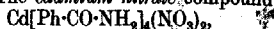
Improved methods were worked out for the preparation of several of the acids. *cyclo*Propanecarboxylic acid was made by a modification of Henry and Dalle's method (A., 1902, i, 525), using  $\alpha$ -dibromopropane in place of  $\alpha$ -chloro- $\gamma$ -bromopropane. *cyclo*Pentanecarboxylic acid was prepared from *2\delta*-dibromobutane, which was made by a modification of Braun and Beschke's method (A., 1907, i, 127).

F. A. M.

**Complexes of Benzamide with Metallic Salts.** L. BELLADEN and R. ASTENGO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 491—493).—Compounds of benzamide with mercury and with silver

were obtained by Tafel and Enoch (A., 1939, 491, 973), and Curtius prepared sodiobenzamide (A., 1891, 58). The authors have now obtained the following complex benzamide compounds, all of which are decomposed by water, with separation of benzamide.

The *cadmium chloride* compound,  $\text{Cd}[\text{Ph}\cdot\text{CO}\cdot\text{NH}_2]\text{Cl}_2$ , and the analogous *cadmium bromide* compound both form slender needles, m. p. above  $450^\circ$ . The *cadmium nitrate* compound,



forms octahedral crystals, m. p.  $194^\circ$ . The *cupric chloride* compound,  $\text{Cu}[\text{Ph}\cdot\text{CO}\cdot\text{NH}_2]\text{Cl}_2$ , forms long, slender, pale green prisms, m. p.  $230^\circ$  (darkening), and dissolves in alcohol to a green solution. The *antimony trichloride* compound,  $\text{SbCl}_3\cdot\text{HCl}[\text{Ph}\cdot\text{CO}\cdot\text{NH}_2]$ , forms long prisms, begins to decompose at about  $70^\circ$  if heated slowly, and melts at  $138^\circ$  if heated rapidly. The analogous *bismuth trichloride* compound crystallises in large, colourless prisms, and, like the antimony compound, may be represented by a structural

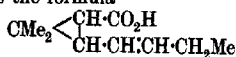
formula of the type, 
$$\begin{array}{c} \text{H} \\ | \\ \text{Cl} \diagup \text{M} \begin{array}{l} \diagdown \text{Cl} \\ \diagdown \text{NH}(\text{HCl})\cdot\text{COPh} \\ \diagdown \text{NH}(\text{HCl})\cdot\text{COPh} \end{array} \end{array}$$
 which is analogous

to that obtained by Bruni and Manuelli (A., 1905, ii, 689) from acetamide and antimony trichloride. T. H. P.

**Lithium, Sodium, Potassium, and Ammonium Hippurates.** C. E. CORFIELD and B. W. MELHUSH (*Pharm. J.*, 1923, 411, 97-98).—The lithium salt is readily obtained in crystalline form; the molecule contains  $2\text{H}_2\text{O}$ . Sodium hippurate is difficult to crystallise from its aqueous solution; the crystals obtained from an alcoholic solution contain  $1.5\text{H}_2\text{O}$  and  $1\text{H}_2\text{O}$  after the salt has been dried over sulphuric acid. A sodium salt containing  $0.5\text{H}_2\text{O}$  could not be prepared. Potassium hippurate ( $1\text{H}_2\text{O}$ ) is deliquescent. Ammonium hippurate is an anhydrous salt, whether crystallised from aqueous or alcoholic solution; it can be prepared most economically by keeping the solution saturated with ammonia during evaporation. When the salt is crystallised from alcoholic solution, it is necessary to treat the solution with twice its volume of ethyl ether in order to induce precipitation. Hippuric acid behaves as a monobasic acid and all attempts to prepare hydrogen salts were unsuccessful. W. P. S.

**The Insecticidal Principle of *Chrysanthemum cinerariaefolium*.** II and III. Constitution of Pyrethronic Acid. RYO YAMAMOTO (*J. Chem. Soc. Japan*, 1923, 44, 311-330; cf. A., 1919, i, 465).—Pyrethron, an effective constituent of *Chrysanthemum cinerariaefolium*, is composed of higher alcohols, an oily substance and a solid and a liquid acid. The liquid acid has a weak effect on insects, but the oily substance none; when, however, the liquid acid was condensed with the oily substance, the ester had almost the same effect as pyrethron itself. The liquid, optically inactive, *pyrethronic acid*,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , b. p.  $110-115^\circ/1\text{ mm.}$ ,  $d\ 0.9685$ ,  $n_D^{20}\ 1.4762$ , was purified by way of its ethyl ester, b. p.  $90-94^\circ/1\text{ mm.}$  When reduced with hydrogen in the presence of

platinum black, a molecule of the acid absorbed two atoms of hydrogen, yielding the saturated acid,  $C_{10}H_{18}O_2$ , which did not crystallise at  $-15^\circ$ . The saturated and unsaturated acids gave barium salts, needles, and the latter a lead salt. The results of analyses of the *amide*, needles, m. p.  $128^\circ$ , and *anilide*, needles, m. p.  $106-107^\circ$ , of pyrethronic acid, and *amide*, m. p.  $133^\circ$ , of the saturated acid showed considerable divergence from those expected from the above formulæ. On oxidising with 1% potassium permanganate solution in sodium carbonate solution at  $0^\circ$ , sodium pyrethronate gave a *dihydroxy-acid*,  $C_9H_{15}(OH)_2CO_2H$ , needles, m. p.  $146^\circ$ , which gave barium and calcium salts. By treating with a mixture of potassium dichromate and sulphuric acid, dihydroxypyrethronic acid gave *trans-caronic acid*,  $CM_2 \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$  needles, m. p.  $212^\circ$ , which gave terepinic acid by heating with acetic anhydride. When pyrethronic acid was ozonised in chloroform solution, caronic acid and its semi-aldehyde were produced; propionic acid and its aldehyde were also detected. The author ascribes the formula



to pyrethronic acid.

K. K.

**Synthesis of Phenylanthranilic Acids.** NEAL TUTTLE (*J. Amer. Chem. Soc.*, 1923, 45, 1906—1916).—*p*-Dimethylaminodiphenylamine is formed by heating *p*'-dimethylaminodiphenylamine-*o*-carboxylic acid above its melting point. The latter is prepared by digesting *o*-chlorobenzoic acid, dimethyl-*p*-phenylenediamine, and potassium carbonate with copper powder in amyl-alcoholic solution; it forms pale green prisms or needles, m. p.  $216^\circ$  (decomp.). It is converted by the action of concentrated sulphuric acid at  $100^\circ$  into 2-dimethylaminoacridone, small, bright yellow clusters, m. p.  $289-290^\circ$ , which shows a green fluorescence in acetic acid solution, but blue in alcoholic sulphuric acid. Dimethyl-*p*-phenylenediamine and 2-chloro-5-nitrobenzoic acid react under similar conditions, or in the presence of copper and aqueous sodium acetate solution, to give *p*-nitro-*p*'-dimethylaminodiphenylamine-*o*-carboxylic acid, small, coppery needles, m. p.  $234-235^\circ$ . Dimethyl-*p*-phenylenediamine and 2-chloro-3:5-dinitrobenzoic acid react in the presence of cold aqueous sodium acetate solution, giving 2:4-dinitro-4'-dimethylaminodiphenylamine-6-carboxylic acid, a bright yellow, amorphous powder, m. p.  $253^\circ$  (decomp.), *hydrochloride*, reddish-brown plates, m. p.  $240-260^\circ$ . Dimethyl-*m*-phenylenediamine condenses with *o*-chlorobenzoic acid, giving *m*'-dimethylaminodiphenylamine-*o*-carboxylic acid, colourless needles, m. p.  $155^\circ$ . With 2-chloro-5-nitrobenzoic acid, the product is *p*-nitro-*m*'-dimethylaminodiphenylamine-*o*-carboxylic acid, small, greenish-brown needles, m. p.  $247^\circ$  (decomp.). The condensation of 2-chloro-1:5-dinitrobenzoic acid with dimethyl-*m*-phenylenediamine may be effected by boiling with alcohol, or with aqueous sodium acetate solution; copper need not be added. The product is 2:4-dinitro-

**3'-dimethylaminodiphenylamine-6-carboxylic acid**, slender, green needles of high melting-point, *hydrochloride*, green needles, which sinter at 320°. **p'-Diethylaminodiphenylamine-o-carboxylic acid** is obtained by the condensation of *o*-chlorobenzoic acid and diethyl-*p*-phenylenediamine; it is a blue solid, which becomes gummy on isolation from the reaction mixture. **p'-Diethylamino-p-nitrodiphenylamine-o-carboxylic acid** forms slender, brown needles, m. p. 239–240°. **4'-Diethylamino-2:4-dinitrodiphenylamine-6-carboxylic acid** is a bright yellow powder, m. p. 259°, *hydrochloride*, orange flakes, m. p. 252–253°; in its preparation, copper need not be employed. **m'-Diethylaminodiphenylamine-o-carboxylic acid** is a dark blue solid, which liquefies when separated from its mother-liquor. The condensation of diethyl-*m*-phenylenediamine with 2-chloro-5-nitrobenzoic acid gives *pp'*-dinitrodiphenyl-*oo'*-dicarboxylic acid. The use of 2-chloro-3:5-dinitrobenzoic acid gives **3'-diethylamino-2:4-dinitrodiphenylamine-6-carboxylic acid**, bright yellow needles, m. p. 220° (decomp.). The action of piperidine on *o*-chlorobenzoic acid in the presence of sodium carbonate, amyl alcohol, and copper powder gives salicylic acid, but the use of 2-chloro-5-nitrobenzoic acid leads to the formation of **5-nitro-2-piperidinobenzoic acid**, very pale yellow, rhombic crystals, m. p. 200–202°. The action of piperidine on 2-chloro-3:5-dinitrobenzoic acid in aqueous sodium acetate solution in the presence of copper powder gives green needles of the *copper salt* of 3:5-dinitrosalicylic acid, which explode violently at about 320°. *o*-Chlorobenzoic acid is unchanged by boiling with 10% aqueous potassium hydroxide solution, and only partial conversion into salicylic acid occurs when amyl-alcoholic potassium hydroxide is used and sodium carbonate and copper powder are added. 5-Nitrosalicylic acid is formed when 2-chloro-5-nitrobenzoic acid is boiled with 10% aqueous potassium hydroxide solution. Aniline and potassium 2-chloro-3-nitrobenzoate condense when boiled in ethyl-alcoholic solution with copper powder, yielding **2-nitrodiphenylamine-6-carboxylic acid**, yellow clusters, m. p. 194°. W. S. N.

**Pharmacological and Clinical Examination of Benzyl Mandelate.** DAVID I. MACHT (*J. Pharm. Expt. Ther.*, 1923, 21, 443–455; cf. *J. Amer. Pharm. Assoc.*, 1923, 12, 7).—Benzyl mandelate forms colourless crystals, m. p. 93°, soluble in the usual organic solvents. A pharmacological and toxicological study of this compound has been made. It shows low toxicity but marked pharmacological activity. W. O. K.

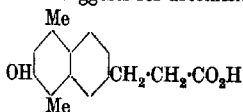
**Attempted Absolute Asymmetric Syntheses.** G. BREDIG [with P. MANGOLD and TH. G. WILLIAMS] (*Z. angew. Chem.*, 1923, 36, 456–458).—A series of attempted syntheses of permanently optically active substances is described in which it was endeavoured to obtain these substances without any assistance whatsoever from other optically active materials, but entirely through the agency of asymmetrical exterior physical forces. The measurement of the dielectric constants and con-

ductivity of hydrocyanic acid and mandelonitrile is described. These measurements were undertaken because it appears there is no chance of the synthesis of an optically active mandelonitrile being effected by carrying out the reaction in an electric field unless the reaction itself is accompanied by a change in the dielectric constant of the material. The measurements indicated that such a change in the dielectric constant does actually take place.

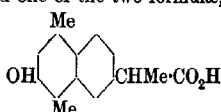
Several attempted asymmetrical syntheses and decompositions with the aid of circularly polarised light are described, the substances acted on being diazocamphor, lactic acid, and asymmetric cobaltamine salts, but in no case was the slightest asymmetry found in the decomposition product. It is considered possible that the effects of circularly polarised rays of a wave-length comparable with the dimensions of the atom might produce the desired results.

H. C. R.

**Chemical Constitution of Artemisic Acid.** P. BERTOLO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 486—490; cf. A., 1920, i, 444, 445).—Two of the three oxygen atoms of the artemisic acid molecule occur in the carboxyl group of the propionic acid residue, whilst the third forms part of the phenolic hydroxyl. Since fusion of artemisic acid with potassium hydroxide yields 1:4-dimethyl- $\beta$ -naphthol, this acid contains unchanged the fundamental nucleus of the artemisin, the ketonic oxygen of the latter being the phenolic oxygen of the acid. The oxygen atom lost as water in the formation of the acid from artemisin is the atom in virtue of which artemisin differs from santonin. Thus, the conversion of artemisin into artemisic acid by treatment with hydrochloric acid involves the elimination of a molecule of water, the rupture of the lactonic linking, and the transformation of the carboxylic oxygen into a phenolic hydroxyl group. On the basis of these considerations the author suggests for artemisic acid one of the two formulæ,



(I.)



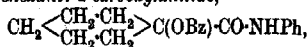
(II.)

Owing to the optical activity of the acid, preference is accorded to formula (II), the analogy between this and the structure ascribed by Gucci and Grassi-Cristaldi to santonic acid (A., 1892, 869) being borne out by the similarity in the methods of formation of the two acids, as well as by physical resemblances. T. H. P.

**isoNitriles. VI. Reaction with Cyclic Ketones in Presence of Organic Acids.** MARIO PASSERINI (*Gazzetta*, 1923, 53, i, 410—417).—*cyclo*Hexanones behave like other ketones when treated with phenylcarbylamine in presence of benzoic acid (cf. A., 1921, i, 743, 895), yielding anilides of 1-benzoyl-*cyclo*hexanol-1-carboxylic acids:  $C_6H_{10}CO + Ph \cdot NC + Ph \cdot CO_2H = C_6H_9C(OBz) \cdot CO \cdot NHPh$ . Good yields of these anilides are readily obtained from *cyclo*hexanone and from the three isomeric methyl-

cyclohexanones. When heated above their melting points, the anilides of 1-benzoylcyclohexanol-1-carboxylic acid and its 3-methyl derivative are converted into isomerides with higher melting points. With each of these two pairs of isomerides, removal of the benzoyl group by hydrolysis results in the formation of a single acid. Hydrolysis of the anilides of 1-benzoyl-2- and 4-methyl-cyclohexanol-1-carboxylic acids yields the anilides of the corresponding non-benzoylated hydroxy-acids, these giving aniline and the hydroxy-acids themselves when subjected to more energetic hydrolysis.

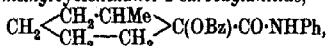
1-Benzoylcyclohexanol-1-carboxylanilide,



forms colourless crystals, m. p. 134—135°, and, when heated above its melting point or boiled in benzene solution, is converted into an isomeride, which forms acicular crystals, m. p. 155—156°, and cannot be reconverted into the original compound by addition of the latter to its solutions.

cycloHexanol-1-carboxylanilide,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}$ , prepared from either of the above isomerides, forms lustrous, white crystals, m. p. 174—175°.

1-Benzoyl-2-methylcyclohexanol-1-carboxylanilide,



forms minute, colourless crystals, m. p. 158—159°.

2-Methylcyclohexanol-1-carboxylanilide,  $\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}$ , crystallises in colourless needles, m. p. 144—146°.

1-Benzoyl-3-methylcyclohexanol-1-carboxylanilide,  $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}$ , forms crystals, m. p. 65°, and, on prolonged heating at 80°, yields an isomeride, m. p. 172—174°, which crystallises unchanged from ethereal solution, but is reconverted into the form of lower melting point when crystallised from alcohol. Hydrolysis of either isomeride gives

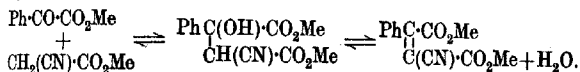
3-Methylcyclohexanol-1-carboxylanilide,  $\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}$ , which crystallises in square plates, m. p. 142—143°. Markownikov and Smirnov (A., 1907, i, 418) prepared this anilide in its *cis*- and *trans*-modifications by the action of aniline on the mixture of the two 3-methylcyclohexanol-1-carboxylic acids prepared from the cyanohydrin of 3-methylcyclohexanone, but both modifications exhibited lower melting points than that now found. 3-Methylcyclohexanol-1-carboxylic acid, described by Markownikov and Smirnov as a vitreous mass, composed of the *cis*- and *trans*-modifications, forms a crystalline mass, m. p. 25—27°.

1-Benzoyl-4-methylcyclohexanol-1-carboxylanilide,  $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}$ , crystallises in minute, colourless needles, m. p. 160—162°.

4-Methylcyclohexanol-1-carboxylonitrile,  $\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}$ , has m. p. 145—146°. T. H. P.

The Mechanism Underlying the Reaction between Aldehydes or Ketones and Tautomeric Substances of the Keto-Enol Type. E. F. KOHLER and B. B. CONSON (J. Amer. Chem. Soc., 1923, 45, 1975—1986).—When methyl benzoylformate and

methyl cyanoacetate, in equivalent proportions, are treated at 0° with a small quantity of ammonia, methylamine, piperidine, or methyl-alcoholic sodium methoxide solution, an equilibrium is rapidly established, with the formation of *methyl β-cyano-α-hydroxy-α-phenylsuccinate*, hexagonal plates, or hard, lustrous, tabular crystals, m. p. 155°, to the extent of 75–80%. This reverts to its components when dissolved in a solution containing any of the above catalysts, and also partly dissociates when distilled under a very low pressure. The action of dehydrating agents, such as boiling glacial acetic acid or phosphoric oxide in phosphorus oxychloride solution, leads, however, to the production of *methyl β-cyano-α-phenylethylene-αβ-dicarboxylate*, large, transparent prisms, m. p. 79–80°, which is also formed if the initial condensation is conducted at the ordinary temperature, or in the presence of a larger quantity of catalyst. It is evident that the effect of the basic condensing agents generally employed in such reactions is dual; they cause condensation, and also bring about elimination of water. These relations are plausibly expressed by the scheme :



There is, however, no proof that the hydroxy-ester is an intermediate product in the formation of the unsaturated ester, because under those conditions which lead to the elimination of water, dissociation can also occur into the components, from which the unsaturated ester may be derived by direct elimination of water. Inasmuch as methyl benzoylformate, which cannot enolise, condenses with methyl cyanoacetate, there is no ground for the assumption that reactions between aldehydes or ketones, and substances containing a mobile hydrogen atom, proceed in general through the enol form of the aldehyde or ketone (Ingold, T., 1921, **119**, 329).

The structure of the unsaturated ester is proved as follows. When it is hydrolysed by means of cold, concentrated, methyl-alcoholic potassium hydroxide solution, the product is *α-cyano-β-phenylmaleic acid*, very pale yellow needles, m. p. about 142° (decomp.), potassium hydrogen salt, colourless needles, m. p. 193–195°, anhydride, yellow needles, m. p. 145–146°. Hydrolysis by boiling with concentrated sulphuric acid and glacial acetic acid gives *α-cyano-β-phenylfumaric acid*, pale yellow crystals, +2H<sub>2</sub>O (lost below 100°), m. p. 158–160°, which sublimes unchanged when heated under reduced pressure. The reduction of the dipotassium salt of this acid in aqueous solution by means of sodium amalgam gives an *amino-acid*, CO<sub>2</sub>H·CHPh·CH(CO<sub>2</sub>H)·CH<sub>2</sub>·NH<sub>2</sub>, m. p. 168–169°, and phenylsuccinic acid. *Methyl α-phenylethane-αββ-tricarboxylate*, needles, m. p. 107–108°, is formed by esterifying the reduction product of the dipotassium salt formed from the unsaturated cyano-ester.

Similar reactions have been conducted using dimethyl malonate. When condensed with methyl benzoylformate, it gives *trimethyl*

*β*-hydroxy-β-phenylethane-αα-tricarboxylate, lustrous prisms, m. p. 109–111°. The corresponding unsaturated ester, *trimethyl β-phenylethylene-αα-tricarboxylate*, is a liquid, b. p. 180–190°/10 mm. The structure of this is proved by hydrolysing it by means of cold, concentrated, alcoholic potassium hydroxide solution, and reducing the resulting potassium salt by means of sodium amalgam to phenylethanetricarboxylic acid, which loses carbon dioxide when heated, and gives phenylsuccinic acid.

W. S. N.

**The Structure of Phenolphthaleinoxime.** W. R. OERDORFF and S. T. YANG (*J. Amer. Chem. Soc.*, 1923, **45**, 1926–1933).—Phenolphthaleinoxime undergoes the Beckmann rearrangement when acetylated or benzoylated, giving the triacetate or dibenzoate of the intermediate product, the *p*-hydroxyanilide of *o*-4'-hydroxybenzoylbenzoic acid (I),  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\langle\text{C}_6\text{H}_4\rangle\text{N}(\text{C}_6\text{H}_4\cdot\text{OH})\rangle\text{CO}$ , +1.5H<sub>2</sub>O,

small, colourless, flaky crystals, m. p. 135° (decomp.). The latter is obtained from the triacetate by hydrolysis by means of cold concentrated sulphuric acid or of cold 4% sodium hydroxide solution. It has a different m. p. when crystallised from different solvents: from acetone, 94–95°; from methyl alcohol, 125°; from ethyl alcohol, 130°; and from ethyl acetate (apparently +0.5MeCO<sub>2</sub>Et), 195–198°. It loses 2.5 molecules of water when heated at 95° in an atmosphere of carbon dioxide, giving a red glass, probably having the structure  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{C}\langle\text{C}_6\text{H}_4\rangle\text{N}(\text{C}_6\text{H}_4\cdot\text{OH})\rangle\text{CO}$ .

The glassy substance dissolves in dilute aqueous alkali solutions, giving a dark green solution from which a yellow, amorphous precipitate separates on acidification. It is assumed that the compound (I) is formed intermediately when phenolphthaleinoxime is hydrolysed by means of dilute sulphuric acid, since when similarly treated it gives the same products, *p*-aminophenol and *o*-4'-hydroxybenzoylbenzoic acid. It gives the same reduction product as the oxime when treated with zinc dust and dilute sulphuric acid; also, like the oxime, it is converted into phenol and *p*-hydroxyphthalanil when heated with a solution of hydroxylamine hydrochloride. The oxime and the intermediate product give the same triacetate when acetylated, and the same dibenzoate when benzoylated; the tribenzoate of the oxime described by R. Meyer and Kissin (*A.*, 1909, i, 651) could not be obtained. When methylated in 30% aqueous sodium hydroxide solution by means of methyl sulphate, the intermediate product gives a colourless *trimethyl ether*, m. p. 131–133°, isomeric with the yellow trimethyl ether formed, by similar treatment, from the oxime. In an attempt to synthesise the intermediate product by fusing *p*-aminophenol with *o*-4'-hydroxybenzoylbenzoic acid, a dark purple solid was obtained. This is probably a mixed phthalein; it dissolves in alkali solutions with formation of a deep purple solution, from which it is reprecipitated by acids. The above results are only explained by means of the formula for phenolphthaleinoxime advanced in an earlier paper (*A.*, 1917, i, 339).

W. S. N.

**4:4'-Dihydroxy-1:1'-dinaphthyl-ketone-3:3'-dicarboxylic Acid.** G. DE MONTMOLIN, J. SPIELER, and G. BONHOTE (U.S. Pat. 1453659; cf. *ibid.*, 1387596).—The action of tetrahalogenomethane derivatives on  $\alpha$ -naphthol-2-carboxylic acid yields, besides a dye, 4:4'-dihydroxy-1:1'-dinaphthyl-ketone-3:3'-dicarboxylic acid, a white powder, decomp. about 259°, and  $\alpha$ -naphthol-2:4-dicarboxylic acid.

CHEMICAL ABSTRACTS.

**Chemical and Optical Behaviour of some dicycloPentane and cycloPentene Derivatives.** N. J. TOIVONEN (*Acta Sci. Fennica*, I, 1922, 26, 1—33; from *Chem. Zentr.*, 1923, i, 1356—1358).—The constitution of the compounds described as cyclopentane derivatives by Perkin and Thorpe (T., 1901, 79, 729) is discussed with reference to the more recent work of the author (*Annalen*, 1919, 419, 176) and of Farmer, Ingold, and Thorpe (T., 1920, 117, 1362; 1922, 121, 128). Their chemical reactions and optical behaviour are considered to be more in accord with the monocyclic (cyclopentene) constitution. It is pointed out that in view of the strain necessitated by the dicyclopentane structure, as high a degree of unsaturation is indicated as by the cyclopentene structure. The following data are given for the compounds in question: Ethyl dicarboxydimethylcyclopropanemalonate, prepared by the method of Perkin and Thorpe (*loc. cit.*), b. p. 203—205°/14 mm.;  $d_4^{20}$  1.1135;  $n_D^{20}$  1.45753;  $R_D$  91.13;  $M \times n_D^{20}$  (Eisenlohr, A., 1921, ii, 1) 542.63. The yellow sodium compound of ethyl 5:5-dimethyldicyclopentane-3-one-1:2:4-tricarboxylate, prepared from methyl dibromodimethylglutarate (1 mol.), ethyl malonate (2 mols.), and sodium ethoxide (4 mols.), has m. p. 208°; the free ester (?) prepared from the last compound by the action on it of dilute sulphuric acid, a viscid liquid, has b. p. 200—212°/14 mm.;  $d_4^{20}$  1.1465;  $n_D^{20}$  1.48742;  $R_D$  81.91;  $M \times n_D^{20}$  485.29. Ethyl 5:5-dimethyldicyclopentane-3-one-1:2:4-tricarboxylate, from the reduction of the above-mentioned yellow sodium compound, is a liquid having b. p. 170—195°/16 mm.;  $d_4^{20}$  1.1202;  $n_D^{20}$  1.46203;  $R_D$  80.56;  $M \times n_D^{20}$  479.94. 1:2-Diethyl 5:5-dimethyldicyclopentane-3-one-1:2:4-tricarboxylate,  $\text{Me}_2\text{C} < \begin{matrix} \text{C}(\text{CO}_2\text{Et}) \\ \text{C}(\text{CO}_2\text{H})-\text{CO} \end{matrix}$  or  $\text{Me}_2\text{C} < \begin{matrix} \text{C}(\text{CO}_2\text{Et}) \\ \text{CH}(\text{CO}_2\text{H})-\text{CO} \end{matrix}$  has m. p. 75°;  $n_D^{20}$  1.49999;  $M \times n_D^{20}$  447.31. Ethyl 2:5:5-trimethyldicyclopentane-3-one-1:2:4-tricarboxylate has b. p. 205—208°/14 mm.;  $d_4^{20}$  1.1250;  $n_D^{20}$  1.47458;  $R_D$  85.09;  $M \times n_D^{20}$  501.77. Ethyl 4:5:5-trimethyldicyclopentane-1-one-1:2:4-tricarboxylate, obtained by reduction of the last compound, is a liquid,  $d_4^{20}$  1.1189;  $n_D^{20}$  1.46155;  $R_D$  84.03;  $M \times n_D^{20}$  500.15. Ethyl 5:5-dimethyldicyclopentane-3-one-1:2-dicarboxylate, obtained by distillation in a vacuum of the 1:2-diethyl ester of 5:5-dimethyldicyclopentane-3-one-1:2:4-tricarboxylic acid, has  $d_4^{20}$  1.1132;  $n_D^{20}$  1.47853;  $R_D$  64.66;  $M \times n_D^{20}$  375.86. Ethyl 5:5-dimethyldicyclopentane-3-one-1:2-dicarboxylate has  $d_4^{20}$  1.0960;  $n_D^{20}$  1.45867;  $R_D$  63.87;  $M \times n_D^{20}$  373.76; the acid corresponding with

the last compound was m. p. 125° (decolorizing  $\alpha$ -ethyl ester of 5:5-dimethyldicyclopentan-3-one-1,2:4-dicarboxylic acid has m. p. 161–162°). Ethyl 5:5-dimethyldicyclopentan-3-one-1-carboxylate is a liquid having b. p. 96°/26 mm.;  $d_4^{20}$  1.0411;  $n_D^{20}$  1.47304;  $R_D$  48.99;  $M \times n_D^{20}$  268.14. G. W. R.

**Derivatives of Phthalonic Acid; 4:5-Dimethoxyphthalonic Acid, and 4:5-Dimethoxy-*o*-tolylglyoxylic Acid.** (Miss) CHIKA KURODA and WILLIAM HENRY PERKIN, jun. (T., 1923, 123, 2094–2111).

**Preparation of Aromatic Aldehydes.** THE BARRETT Co. (Brit. Pat. 189107).—Monoaldehydes are produced by catalytic oxidation of aromatic hydrocarbons containing a benzene nucleus in which at least two hydrogen atoms have been substituted, one at least of the substituents being an alkyl group. The vapour of the hydrocarbon, mixed with an oxygen-containing gas (e.g., air) is passed over a metallic oxide, other than vanadium oxide, of the fifth or sixth periodic group. The reaction temperature is between 300° and dull redness, and the time of contact in the neighbourhood of 0.3 seconds. Acid formation is negligible. Vanadium oxide differs from the other oxides specified in oxidising the aliphatic side-chain to the acid stage and even causing disruption of the aromatic nucleus itself. The production of monoaldehydes from *o*-, *m*-, and *p*-xylene,  $\psi$ -cumene, mesitylene, *p*-cymene, and of *o*-chlorobenzaldehyde from *o*-chlorotoluene, is described, the yields varying from 17% ( $\psi$ -cumene) to 63% (*o*-chlorotoluene). W. T. K. B.

**The Isomerism of the Oximes. XIII. Phenylethyl-, Diethyl-, and  $\alpha$ -Naphthyl-carbamyl Derivatives.** OSCAR LASLE BRADY and DUDLEY RIDGE (T., 1923, 123, 2163–2174).

**4-Methoxyresorcyraldehyde [2-Hydroxy-4-methoxybenzaldehyde]** from the Roots of *Decalepis Hamiltonii*. M. G. SRINIVASA RAO and M. SESA IYENGAR (Perf. Essent. Oil Rev., 1923, 14, 300–301).—When the crushed roots of *Decalepis Hamiltonii* are distilled in steam with a little animal charcoal, there is obtained a white, crystalline solid, m. p. 41°, which possesses an odour resembling that of vanillin. This compound is shown to be 2-hydroxy-4-methoxybenzaldehyde. H. H.

**New Isomeride of Wieland's Dibenzenyloxazoxime.** E. PARISI (Atti R. Accad. Lincei, 1923, [v], 32, i, 572–575).—Two compounds of the formula  $C_{14}H_{10}O_2N_2$  have been obtained by oxidation of benzaldoxime, namely, so-called diphenylglyoxime peroxide (cf. Scholl, A., 1891, 316), and dibenzenyloxazoxime (cf. Wieland and Bauer, A., 1906, i, 412; 1907, i, 527). The author finds that oxidation of benzaldoxime by means of iodine and alkali (cf. Robin, A., 1919, i, 592) yields dibenzenyloxazoxime, m. p. 135°, together with a third isomeride,  $C_{14}H_{10}O_2N_2$ , which crystallises in stellate groups of laminae, m. p. 63°; either of these isomerides yields dibenzenyloxime when reduced by means of zinc and

acetic acid. With iodine the two isomerides, m. p. 135° and 63°, respectively, form additive compounds, m. p. 140° and 151°, respectively.

Diphenylglyoxime peroxide, however, yields no additive compound with iodine, and when reduced by means of zinc and acetic acid, gives diphenylfurozan,  $\text{O} \begin{smallmatrix} \text{N} \cdot \text{CPh} \\ \text{N} \cdot \text{CPh} \end{smallmatrix}$ , which may be regarded

as a product of anhydride formation with benzildioxime. It is therefore probable that the peroxide has the formula  $\text{O} \begin{smallmatrix} \text{N} \text{---} \text{CPh} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{N} \text{---} \text{CPh} \end{smallmatrix}$

or  $\text{O} \cdot \text{N} \cdot \text{CPh}$ . The other two isomerides contain the nucleus  $\text{O} \begin{smallmatrix} \text{N} \cdot \text{C} \\ \text{C} \cdot \text{N} \end{smallmatrix}$  and the constitution proposed by Wieland for the compound, m. p. 135°,  $\text{O} \begin{smallmatrix} \text{N} \cdot \text{CPh} \\ \text{CPh} \cdot \text{O} \end{smallmatrix} \text{N}$ , is supported by its sensitiveness towards the influence of light. The isomeride, m. p. 63°, has probably the structure  $\text{O} \begin{smallmatrix} \text{NO} \text{---} \text{CPh} \\ \text{CPh} \cdot \text{N} \end{smallmatrix}$ .

T. H. P.

**Ring Formation from  $\gamma$ -Ketonic Esters.** CLAUDE LE PELETIER DE ROSANBO (*Ann. Chim.*, 1923, [ix], 19, 327—355).—The formation of a cyclic compound from a  $\gamma$ -ketonic ester was effected by using the ethyl ester of  $\beta\beta$ -trimethyl-lævulic acid, in which the two hydrogen atoms in the  $\beta$ -position are substituted and reaction of the enolic form of the ester is thus obviated. The action of sodium ethoxide on this substance yields 1 : 1 : 3-trimethyl-cyclopentane-2 : 4-dione,  $\text{C}_8\text{H}_{12}\text{O}_2$ , white needles, m. p. 163°, b. p. 180°/10 mm.,  $d_4^{20}$  0.83901,  $n_D^{25}$  1.38949, monoacetyl derivative, b. p. 124°/21 mm., phenylhydrazone, white needles, m. p. 229°. A mixture of two isomeric methyl derivatives was obtained, but neither was separated in the pure condition. It was not found possible to prepare cyclic compounds from the ethyl esters of lævulic,  $\beta$ -methyl-lævulic, or  $\alpha\alpha\delta$ -trimethyl-lævulic acids.

H. J. E.

**Dioximes.** XI. G. PONZIO (*Gazzetta*, 1923, 53, i, 379—384).—If the compound obtained by the action of nitrogen tetroxide on phenylglyoxime (cf. this vol., i, 472) possesses the phenylfuroxan structure attributed to it by Wieland and Semper (*A.*, 1908, i, 108) it should, in accordance with the results of Forster and Barker (*T.*, 1913, 103, 1918), Green and Rowe (*T.*, 1913, 103, 897, 2023), and Angeli (*A.*, 1916, i, 655) and in virtue of its unsymmetrical ring, be capable of existing in two modifications. That the latter actually exist is stated by Wieland (*A.*, 1921, i, 605), who describes an unstable form of phenylfuroxan, m. p. 106—108°, the ordinary, stable form having m. p. 96—97°.

The author finds that only one compound of the formula  $\text{C}_2\text{HPhO}_2\text{N}_2$  exists, that it melts at either 95° or 96—97° or 108°, according to its degree of purity, and that its behaviour towards hydrochloric acid, acetic anhydride, and nascent hydrogen indicates

it to be neither phenylglyoxime peroxide nor phenylthioxan, but the oxide of benzoyl cyanide oxime (oximinobenzoyl cyanide oxide),

$\text{NOH:CPh-C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{N} \end{smallmatrix}$ . In the pure state, this compound has m. p.

$108^\circ$  and exhibits the normal molecular weight in acetic acid. It is converted completely into benzonitrile, benzoic acid, and hydroxylamine when subjected to prolonged boiling with concentrated hydrochloric acid, and it yields an acetyl derivative,

$\text{NOAc:CPh-C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{N} \end{smallmatrix}$ , crystallising in white needles, m. p.  $115-116^\circ$ .

When reduced with zinc dust and acetic acid, it yields benzoyl cyanide oxime.

This structure for the compound explains the formation of aminophenylglyoxime when it is treated with aqueous ammonia (this vol., i, 472), and that of anilinophenylglyoxime when treated with aniline (this vol., i, 855). As regards the mechanism of its formation, it has been shown that the two oximino-groups of the  $\alpha$ -forms of the glyoximes are not equivalent, and it is assumed that  $\alpha$ -phenylglyoxime reacts with nitrogen tetroxide as its tautomeride,  $\alpha$ -oximino- $\beta$ -nitroso- $\alpha$ -phenylethane,  $\text{NOH:CPh-CH}_2\text{NO}$ , giving  $\alpha$ -oximino- $\beta$ -nitrophenylethane,  $\text{NOH:CPh-CH(ONO)NO}_2$ . The latter, being unstable, would then yield the oxide of benzoyl cyanide oxime by loss of nitrous acid.

T. H. P.

**Piperitone. V. The Characterisation and Racemisation of l-Piperitone.** JOHN READ and HENRY GEORGE SMITH (T, 1923, 123, 2267-2272).

**Hydroxynaphthaquinone. VI. The Chlorination of Juglone.** ALVIN S. WHEELER, P. R. DAWSON, and JOSEPH L. McEWEN (J. Amer. Chem. Soc., 1923, 45, 1970-1975).—The best conditions are described for the preparation of dichlorojuglone (A., 1919, i, 490) by the chlorination of juglone in glacial acetic acid solution at  $100^\circ$ . Attempts to prepare a trichloro-derivative have only led to the formation of the same dichlorojuglone. It forms an indigo-blue sodium salt, which gives a deep violet, aqueous solution from which silk and wool may be dyed buff and brown shades. 2:3-Dichloro-5-benzoyl-1:4-naphthaquinone, pale yellow, needles, m. p.  $225^\circ$ , is prepared by boiling dichlorojuglone with benzoyl chloride. Dichlorojuglone is converted by the action of boiling alcoholic sodium hydroxide solution into 3-chloro-2:5-dihydroxy-1:4-naphthaquinone, golden-brown needles, m. p.  $191^\circ$ , which gives a deep red, aqueous solution changing to yellow on addition of acid (diacetate, slender, yellow needles, m. p.  $147^\circ$ ). This chlorodihydroxy-derivative is also produced by the action of sodium ethoxide on dichlorojuglone in benzene solution. Dichlorojuglone reacts in boiling alcoholic solution with aniline, *p*-chloroaniline, or *p*-toluidine, but not with 2:4-dichloroaniline, to give, respectively, 3-chloro-2-anilino-5-hydroxy-1:4-naphthaquinone, very small, short, flat, lustrous, violet-carmine needles, m. p.  $222^\circ$ ; 3-chloro-2-*p*-chloro-anilino-5-hydroxy-1:4-naphthaquinone, flat, dark reddish-purple

needles, m. p. 249°, or 2-chloro-2-p-toluidino-5-hydroxy-1:4-naphthaquinone, flat, lustrous, dark reddish-purple needles, m. p. 234°. Reduction of dichlorojuglone by treating its ethereal solution with dilute sulphuric acid and zinc dust gives 2:3-dichloro-1:4:5-trihydroxynaphthalene, very small, short, lustrous, grey prisms, m. p. 157° (decomp.), triacetate, pale yellow, transparent needles, m. p. 182°. An oxime of dichlorojuglone has not been obtained.

W. S. N.

**Preparation of 1- and 2-Nitro-derivatives of Anthraquinone and its Substitution Products.** EDUARD KOPETSCHNI (D.R.P. 363930; from *Chem. Zentr.*, 1923, ii, 1029—1030).—Aminoanthraquinones are treated with per-acids and the products are also submitted to oxidation with another oxidising agent. By the oxidation of 2-aminoanthraquinone with persulphuric acid, 2-nitroanthraquinone may be obtained directly. The reaction is also applicable to substitution products of aminoanthraquinone. By the action of persulphuric acid or Caro's acid on 1-aminoanthraquinone or its 4-chloro-substitution product, nitroso-compounds are first formed which may be oxidised to nitroanthraquinones by means of chromium trioxide. For example, 2-aminoanthraquinone, dissolved in strong sulphuric acid is added to an aqueous solution of ammonium persulphate and the mixture finally heated at 100°. Addition of acetic acid facilitates the reaction through formation of peracetic acid. The 2-nitroanthraquinone is obtained as yellow needles, m. p. 181—182°. 1-Chloro-2-nitroanthraquinone, similarly obtained, forms yellow needles, m. p. 257—258°. On being heated with copper powder in nitrobenzene solution, it gives 2:2'-dinitro-1:1'-dianthraquinonyl, yellow prisms, m. p. 342° (decomp.). Reduction with sodium hyposulphite in alkaline solution gives flavanthren. By treating 4-chloro-1-aminoanthraquinone, dissolved in strong sulphuric acid, with ammonium persulphate, 4-chloro-1-nitrosoanthraquinone is first obtained; it forms golden-yellow leaflets, m. p. 240° (decomp.). This, by oxidation with chromium trioxide in boiling acetic acid, yields 4-chloro-1-nitroanthraquinone, sulphur-yellow needles, m. p. 260—261°. By successive oxidation of 1-aminoanthraquinone with Caro's acid and chromium trioxide, 1-nitroanthraquinone, m. p. 227—228°, is obtained. G. W. R.

**Preparation of 1:1'-Dianthraquinonyl and its Derivatives.** EDUARD KOPETSCHNI (D.R.-PP. 360419 and 362984; from *Chem. Zentr.*, 1923, ii, 1030).—Dianthraquinonyl 1:1'-disulphide, 1-anthraquinone thiocyanate, or their substitution products, are heated with metals, such as copper or iron, which combine with sulphur. For example, by heating dianthraquinonyl disulphide or anthraquinone 1-thiocyanate with copper and anthracene at 220—240°, 1:1'-dianthraquinonyl is obtained as brownish-yellow crystals, m. p. 430°. From 2:2'-dimethyldianthraquinonyl 1:1'-disulphide, 2:2'-dimethyl-1:1'-dianthraquinonyl is obtained; it forms yellow crystals and, when heated with alcoholic potassium hydroxide, gives pyranthrone. 2:2'-Dihydroxy-1:1'-dianthraquinonyl, to-

gether with 2-hydroxyanthraquinone, is obtained by a similar reaction. G. W. R.

**Camphor Series. III. Catalytic Action of Reduced Copper on *d*-Camphoroxime.** SHIGERU KOMATSU and SHOU YAMAGUCHI (*Mem. Coll. Sci. Kyoto*, 1923, 6, 245-250; cf. this vol., i, 234).—When *d*-camphoroxime is reduced by means of hydrogen and reduced nickel, bornylamine is formed (Aloy and Brustier, A., 1911, i, 730). With reduced copper at 200°, however, a molecular rearrangement occurs, and the products are levorotatory *d*- $\alpha$ -campholenamide,  $\alpha$ -campholenic acid, *d*-camphor,  $\alpha$ -campholenonitrile, and only a trace of bornylamine. The authors therefore conclude that the oxime is converted into the isooxime by the rupture of a cyclopentane ring, and that this is followed by the decomposition of the isooxime to give campholenamide. H. H.

**The Reaction between  $\alpha$ -Pinene and Acids. I.  $\alpha$ -Pinene and Sulphuric Acid.** KASHICHI ONO (*Mem. Coll. Sci. Kyoto*, 1923, 6, 306-311).—The influence of time, temperature, and concentration of acid on the reaction between pinene and sulphuric acid was studied. The optimum conditions for the formation of terpin hydrate are attained when pinene and three times its weight of 45% sulphuric acid are allowed to react at a temperature in the neighbourhood of 0°. A scheme is proposed to represent the catalytic hydration of pinene. H. H.

**New Syntheses from Hydrocyanic Acid by Means of the Silent Electric Discharge. Behaviour of Pinene.** LUIGI FRANCESCONI and ADOLFO CIURLO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 566-569; *Gazzetta*, 1923, 53, 470-472; cf. this vol., i, 764).—Under the influence of the silent discharge, pinene vapour and hydrogen cyanide interact at 50°, yielding a nitrile and an isonitrile, the latter in predominating proportion. At lower temperatures the hydrogen cyanide condenses in the ozoniser and undergoes change under the influence of the discharge, whilst at higher temperatures the pinene gives a dense, resinous product and the amount of isonitrile formed diminishes, to vanish at 130°. T. H. P.

**The Essential Oil in the Leaves of *Dacrydium biforme*.** BASIL HUGHSON GOUDIE (*J. Soc. Chem. Ind.*, 1923, 42, 357-358r).—Leaves of the conifer, *D. biforme*, when extracted by treatment with superheated steam, yield 0.25% of a pale green oil, *d* 0.8876, *n*<sub>D</sub> 1.5,  $\alpha$  -11.96°, together with a small quantity of a crystalline compound. The oil was separated into three fractions by distillation. The first, b. p. 130-140°/13 mm., had *d* 0.916, *n*<sub>D</sub> 1.505,  $\alpha$ <sub>D</sub> -54.9°, and was probably cadinene. The second, b. p. 140-185°/13 mm., consisted mainly of an oxygenated compound. The third, highest boiling fraction, solidified on cooling. It crystallises from benzene in colourless plates, m. p. 91°, and is a diene with one ethylene linking, C<sub>20</sub>H<sub>32</sub>, for which the name *dacrene* is suggested. It has  $\alpha$  +14.9° and forms a dibromide, m. p. 110°. H. H.

**The Essential Oils in the Leaves of *Librocedrus Bidwilli*.**  
 BASIL HUGHSON GORDON (*J. Soc. Chem. Ind.*, 1923, 42, 350—351).  
 —The leaves of *Librocedrus Bidwilli* when distilled with superheated steam give a greenish-yellow oil,  $d$  0.8754,  $n_D$  1.845, having the composition  $C_{10}H_{16}$ . The yield varies from 0.62% from older, to 0.42% from younger trees. The oil consists of about 30% of terpenes, of which  $\alpha$ -pinene is the chief constituent, and 70% of sesquiterpenes. The original oil was laevorotatory, but when fractionated at the ordinary pressure the fractions were dextrorotatory. Fractionation at low pressure, however, gave a sesquiterpene fraction, b. p. 120—130°/12 mm.,  $d$  0.887;  $n_D$  1.50,  $\alpha_D$  -74.6°. This could not be identified with either of the known laevorotatory sesquiterpenes, cadinene and cedrene. E. H. R.

***Thevetia nerifolia*, Juss.** R. WEITZ and A. BOULAY (*Bull. Sci. Pharmacol.*, 1923, 30, 81—88; from *Chem. Zentr.*, 1923, i, 1328).—The glucoside extracted from *Thevetia nerifolia*, Juss., has a bitter taste. It gives with sulphuric acid an ochre-yellow coloration, becoming pink after twelve hours. A yellow coloration is given with nitric acid. When heated with resorcinol and hydrochloric acid a pink coloration is obtained. G. W. R.

**New Sources of Santonin.** ARNO VIEHOEVEER and RUTH G. CAPEN (*J. Amer. Chem. Soc.*, 1923, 45, 1941—1944).—Of fifty-six species of *Artemisia* indigenous to America, pronounced tests for santonin were obtained from *A. mexicana*, Willd., from *A. neo-mexicana*, Wooton, and probably from *A. Wrightii*, all of which grow in the region of New Mexico and Mexico. W. S. N.

**The Action of Organomagnesium Compounds on Cyano-hydrins. I. A New Method for the Preparation of Substituted Benzoin.** YASUHIKO ASAHINA and MASANOBU TERASAKA (*J. Pharm. Soc. Japan*, 1923, No. 494, 219—228).—Aromatic organomagnesium compounds combine fairly smoothly with aromatic aldehyde cyanohydrins in ethereal solution; from the products, substituted benzoin is obtained by decomposition with water and dilute sulphuric acid:  $R\cdot CH(OH)\cdot CN + 2R\cdot MgX \rightarrow R\cdot CH(OMgX)\cdot CR\cdot NMgX \rightarrow R\cdot CH(OH)\cdot COR$ . Benzoin was thus prepared from benzaldehyde cyanohydrin and magnesium-phenyl bromide, the yield being 32.7% of the theoretical. Benzofuroin,  $C_6H_5O\cdot CH(OH)\cdot CPh$  (1 g.), colourless prisms, m. p. 119°, was prepared from furfuraldehyde cyanohydrin and magnesium-phenyl bromide. It is an isomeride of Fischer's benzofuroin (*Annalen*, 1882, 211, 288), and its oxidation with Fehling's solution produced benzofuril,  $CO\cdot Ph\cdot CO\cdot C_6H_5O$ , m. p. 41°, identical with that of Fischer. *p*-Methoxybenzoin,  $OMe\cdot C_6H_4\cdot CH(OH)\cdot CPh$  (3 g.), was prepared from anisaldehyde cyanohydrin (5 g., m. p. about 62°) and magnesium-phenyl bromide as colourless prisms, m. p. 89°. *o*-Hydroxybenzoin,  $OH\cdot C_6H_4\cdot CH(OH)\cdot CPh$ , prepared from magnesium-phenyl bromide and salicylaldehyde cyanohydrin, forms colourless plates from alcohol and has m. p. 143°. *o*-Methoxy-

benzoin (5 g.),  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{COPh}$ , was obtained from magnesium phenyl bromide and *o*-methoxysalicylaldehyde cyanohydrin (8.2 g.), as colourless prisms, m. p. 58°. On oxidation with Fehling's solution, the benzoin gave *o*-methoxybenzil, slightly yellow prisms, m. p. 71.5°, which was changed by warming with alkali into *o*-methoxybenzilic acid, colourless needles (+2EtOH), m. p. 100–101°, and giving a dark red colour with concentrated sulphuric acid. *op*'-Dimethoxybenzoin,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , (3.8 g.), was prepared from magnesium *p*-methoxyphenyl bromide and *o*-methoxysalicylaldehyde cyanohydrin (8 g.), as colourless prisms, m. p. 92–93°. By oxidising with Fehling's solution, the benzoin gave *op*'-dimethoxybenzil, fine, colourless prisms, m. p. 104–105°, which was converted by alkali into *op*'-dimethoxybenzilic acid, m. p. 162°. K. K.

Triethylene Tri- and Tetra-sulphides. III. The Sulphonés, Sulphinic, and Sulphonic Acids of the Series. Extension of Stuffer's Law. (SIR) PRAFULLA CHANDRA RAY (T., 1923, 123, 2174–2178).

The Preparation of *N*-Derivatives in the Carbazole Series. THOMAS STEVENS STEVENS and STANLEY HORWOOD TUGER (T., 1923, 123, 2140–2147).

Derivatives of Tetrahydrocarbazole. III. Amino-compounds. GEORGE ALFRED EDWARDS and SYDNEY GLENN PRESTON PLANT (T., 1923, 123, 2393–2399).

Oxidation of Benzylidenemethylisooxazolone. MARIO BETTI and NATALIA VIANISINO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 494–498).—It has been shown (A., 1922, i, 52) that oxidation by means of atmospheric oxygen of 4-benzylidene-3-methylisooxazolone, dissolved in alcoholic ammonia containing benzaldehyde, gives an amide which yields an unstable acid,  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ , or an isomeric stable acid, according as it is hydrolysed by dilute or by concentrated sodium hydroxide solution. When, however, the oxidation is effected in ammoniacal alcoholic solution by means of hydrogen peroxide, the product is the ammonium salt of an acid,  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ , whereas in aqueous ammonia a different compound, m. p. 120°, is obtained.

The free acid,  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ , forms minute, lustrous crystals, m. p. 131° (decomp.), and the ammonium salt,  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N} \cdot \text{NH}_4 + 0.5\text{H}_2\text{O}$ , massive, lustrous crystals, m. p. 157° (decomp.); the silver salt was analysed.

Oxidation of 4-*p*-chlorobenzylidene-3-methylisooxazolone in alcoholic ammonia solution by means of hydrogen peroxide gives the ammonium salt,  $\text{C}_{11}\text{H}_9\text{O}_4\text{NCl} \cdot \text{NH}_4 \cdot 2\text{H}_2\text{O}$ , which forms small, white crystals, m. p. 165°. T. H. P.

Oxidation of Isooxazolone Compounds. MARIO BETTI and NATALIA VIANISINO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 563–566; cf. preceding abstract).—Oxidation of 3-phenyl-4-benzylideneisooxazolone in alcoholic ammonia solution by means of hydrogen

peroxide proceeds similarly to that of 4-benzylidene-3-methylisoxazolone under the same conditions, the only difference being that the amide and not the ammonium salt is obtained in the present case.

This *amide*,  $\text{NO}_2\text{-CHPh-C}(\text{CHPh})\text{-CO-NH}_2(?)$ , forms lustrous, white, acicular crystals, m. p.  $232^\circ$ . The corresponding *acid*,  $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}$ , forms white, acicular crystals, m. p.  $118^\circ$ , and exhibits the normal molecular weight in freezing benzene. T. H. P.

**Studies in the Benzothiazole Series. I. The Pseudo-bases of the Benzothiazole Quaternary Salts.** WILLIAM HOBSON MILLS, LESLIE MARSHALL CLARK, and JOHN ALFRED AESCHLMANN (T., 1923, 123, 2353—2362).

**Studies in the Benzothiazole Series. II. Thio-2-methylbenzothiazolone and its Oxidation Products.** WILLIAM HOBSON MILLS, LESLIE MARSHALL CLARK, and JOHN ALFRED AESCHLMANN (T., 1923, 123, 2362—2370).

**Dyestuffs Derived from Heterocyclic Bases containing Reactive Methyl Groups.** JAMES LEONARD BRIERLEY SMITH (T., 1923, 123, 2288—2296).

**Condensation of Amidines with Ethoxymethylene Derivatives of  $\beta$ -Ketonic Esters and of  $\beta$ -Diketones.** PRAFULLA CHANDRA MITTER and JOGENDRA CHANDRA BARDHAN (T., 1923, 123, 2179—2184).

**Compounds of Diketopiperazines and Amino-acids or Polypeptides.** EMIL ABDERHALDEN and EMIL KLARMANN (Z. physiol. Chem., 1923, 129, 320—324).—By the action of chloroacetyl chloride on glycine anhydride in nitrobenzene solution, 1:4-di(chloroacetyl)-2:5-diketopiperazine is obtained, white scales, m. p.  $168.5^\circ$ . On treatment with alcoholic ammonia, 1:4-diglycylglycine anhydride is obtained, colourless leaflets, decomp. above  $220^\circ$ . This substance gives the biuret reaction, and its solution becomes cloudy on the addition of phosphotungstic acid.

W. O. K.

**Benzisthiazoles. IV.** STEPHEN RATHBONE HOLDEN EDGE (T., 1923, 123, 2330—2333).

**Studies in Phototropy. The Reversed Phototropy of Cinnamaldehydesemicarbazone and its Methoxy-derivatives.** ISIDOR MORRIS HEILBRON, HERBERT EDWARD HUDSON, and DORIS MABEL HUISE (T., 1923, 123, 2273—2279).

**Triazole Compounds. I. Some Substituted Hydroxybenzotriazoles and their Methylation Products.** OSCAR LESLIE BRADY and JAMES NELSON EDMUND DAY (T., 1923, 123, 2258—2267).

**6:6'-Diacetylamino-1:1'-diethylcarbocyanine Iodide.** FRANCES MARY HAMER (T., 1923, 123, 2333—2336).

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**Formation of certain Azides.** A. ANGELI and ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 450—455).—The formula  $\text{NH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$  is improbable for the compound, m. p.  $71^\circ$  (this vol., i, 612), since the latter readily yields derivatives of triazole, the ring of which contains a direct chain of three nitrogen atoms. This reaction has been shown by Dimroth (A., 1902, i, 403) to be characteristic of the azides, and the conclusion is drawn that the above compound is diphenylamine-4-azide,  
 $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{N}$ .

As regards the mode of formation of this compound, true nitroso-derivatives react with hydroxylamine to furnish diazo-hydroxides,  $\text{C}_6\text{H}_5\cdot\text{NO} \rightarrow \text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{OH}$ , but in alkaline solution *p*-nitrosodiphenylamine may be regarded as containing the oximino-group,  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NOH}$ . It must therefore be assumed that the hydroxylamine is first added to the double quinonoid linking to give a diazo-compound possibly identical with that described by Hantzsch,  $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$  (A., 1902, i, 324). This product would then react with a second molecule of hydroxylamine to give the azoimide derivative. No reaction analogous to this has, however, been observed.

Diphenylamine-4-azide forms pale yellow or reddish-yellow crystals and in most of its reactions decomposes with formation of intensely coloured or resinous products. When poured into concentrated sulphuric acid, it reacts violently with evolution of much gas; with concentrated nitric acid, it explodes with emission of flame. An acetic acid solution of nitric acid converts it into a reddish-brown product, m. p.  $84^\circ$  (decomp.), as yet not investigated further. It is extremely sensitive to the action of light, and yields an almost colourless, crystalline hydrochloride. Nitrous acid converts it into the *nitrosoamine*,  $\text{C}_{12}\text{H}_{10}\text{ON}_3$ , which crystallises in lustrous, yellow laminae, m. p.  $55^\circ$ , explodes when heated on platinum, yields an intense Liebermann's reaction, and gives the original azide when treated with hydroxylamine hydrochloride in acetic acid solution.

The compound,  $\text{NHR}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} < \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{Et} \\ \text{N}=\text{N} \end{smallmatrix}$ , obtained by the action of ethyl acetoacetate on diphenylamine-4-azide, crystallises in colourless prisms, m. p.  $170^\circ$ . The free acid,  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_4$ , forms colourless crystals, m. p.  $208^\circ$ , the compound losing carbon dioxide at this temperature with formation of the triazole, which separates in colourless crystals, m. p.  $123^\circ$ . T. H. P.

**Bromination of 2-Amino-*p*-xylene and certain New Azo-dyes.** ALVIN S. WHEELER and E. W. CONSTABLE (*J. Amer. Chem. Soc.*, 1923, 45, 1999—2001).—The bromination of 2-acet-amido-*p*-xylene in cold glacial acetic acid solution gives 5-bromo-2-acetamido-*p*-xylene, rosettes of colourless needles, m. p.  $187^\circ$ , which, when hydrolysed by means of concentrated hydrobromic acid, *d* 1-3, is converted into the *hydrobromide*, flat needles, m. p.  $255^\circ$  (decomp.), of 5-bromo-2-amino-*p*-xylene (Fischer and Windhaus, A., 1900, i, 484). The constitution of the latter is fixed by

its conversion into the known 2:5-dibromo-*p*-xylene, by diazotisation, followed by treatment with copper powder and potassium bromide. This proof is extended by the oxidation of 2:5-dibromo-*p*-xylene, by heating at 300° with nitric acid, *d* 1.15, to 2:5-dibromoterephthalic acid.

Azo-dyes have been prepared by diazotising 5-bromo-2-amino-*p*-xylene, and coupling with phenols. When phenol, resorcinol, or  $\alpha$ -naphthol is used, a bis-compound is formed, but not with  $\beta$ -naphthol. Owing to difficulty in making the sodium salts, the tinctorial properties on silk and wool are found by employing the development method of application. 2:4-Bis(5'-bromo-2'-*p*-xylylazo)phenol forms small, dark brown scales with a metallic lustre, which appear pale green under the microscope, *m. p.* 233–234°. Silk is coloured *écru*, and wool, orange-brown. 2:4-Bis(5'-bromo-2'-*p*-xylylazo)resorcinol, a microcrystalline, claret-brown mass, *m. p.* 263°, dyes silk *écru* and wool Brazil-red. 2:4-Bis(5'-bromo-2'-*p*-xylylazo) $\alpha$ -naphthol, a dark brown or black mass, *m. p.* 222–223°, dyes silk a Mars-orange and wool a claret-brown. 1:5'-Bromo-2'-*p*-xylylazo- $\beta$ -naphthol forms long, scarlet-red needles in felted masses, and colours silk a light red and wool a Nopal-red.

W. S. N.

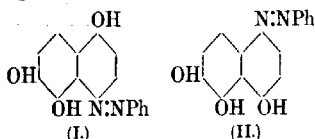
**Asymmetric Dyes.** C. W. PORTER and HARRY K. IHRIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1990–1993).—Two new series of asymmetric dyes are described. The members of the first group are made by producing asymmetric amines through the condensation of bromo-acid bromides with acetanilide, then diazotising these products and coupling with aromatic amines or phenols. Those of the second class are prepared by diazotising aminomandelic acid, and coupling with aromatic amines or phenols. *p*-Azo- $\beta$ -naphtholmandelic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , is a bright red dye, *m. p.* 118°, from diazotised *p*-aminomandelic acid and  $\beta$ -naphthol. *p*-Azoresorcinolmandelic acid,

$\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , *m. p.* 154° (decomp.), is a red dye. *p*-Azodimethylaminomandelic acid,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , *m. p.* 125–129° (decomp.), is brown, but bright red in acid solution. *m*-Azoresorcinolmandelic acid, *m. p.* above 280°, is a red dye. *m*-Azodimethylaminomandelic acid, *m. p.* 158°, is reddish-purple. *m*-Azophenolmandelic acid, *m. p.* 119°, is a bright yellow compound.  $\beta$ -Naphtholazo- $\alpha$ -hydroxypropionophenone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , *m. p.* 132°, is a red dye made by condensing  $\alpha$ -bromopropionyl bromide with acetanilide, hydrolysing the product, diazotising the resulting *p*-aminopropionophenone, and coupling with  $\beta$ -naphthol.  $\beta$ -Naphtholazo- $\alpha$ -hydroxybutyropenone, *m. p.* 72°, is a red dye, made from *p*-aminobutyropenone and  $\beta$ -naphthol.  $\beta$ -Naphtholazo- $\alpha$ -hydroxyisovalerophenone is a red dye, *m. p.* above 265°, derived from the condensation product of  $\alpha$ -bromoisovaleryl bromide and acetanilide, by hydrolysis, diazotisation, and coupling with  $\beta$ -naphthol.

The cinchonine salt of *m*-aminomandelic acid has *m. p.* 156.5°.

By fractional crystallisation of this salt, and subsequent treatment with hydrochloric acid, *d-m-aminomandelic acid*, m. p.  $130^{\circ}$  (decomp.),  $[\alpha]_D +33.80^{\circ}$  and *l-m-aminomandelic acid*, m. p.  $130^{\circ}$  (decomp.),  $[\alpha]_D -33.65^{\circ}$ , are obtained. By diazotising these acids at  $0^{\circ}$ , and coupling in alkaline solution with  $\beta$ -naphthol, *d-m-azo- $\beta$ -naphtholmandelic acid* and *l-m-azo- $\beta$ -naphtholmandelic acid* are prepared. Each is a red dye, m. p.  $210^{\circ}$ ,  $[\alpha]_D \pm 49^{\circ}$  ( $\pm 5^{\circ}$ ). These dyes do not attach themselves equally readily to wool or silk; the dextro-form is more rapidly removed from solution. Hence if dyeing is conducted from a solution of the racemic mixture of the dyes, the unused dye is optically active. By using an excess of wool and extending the time of contact to seventy-two hours, the residual dye is almost a pure levorotatory compound. Thus selective absorption by wool of an optically active dye is definitely established (cf. Porter and Hirst, A., 1919, i, 558). W. S. N.

**Naphthazarin (5:6-Dihydroxy-1:4-naphthaquinone).** G. CHARRIER and G. TOCCO (*Gazzetta*, 1923, 53, i, 431—436).—Like 1:4-naphthaquinone (cf. Zincke and Bindewald, A., 1885, 391), naphthazarin reacts with phenylhydrazine (1 mol.) in presence of



acetic acid, giving rise to the benzeneazo-derivative of a trihydroxynaphthalene of the annexed formula I or II. No decision between these structures is yet possible, since the two corresponding trihydroxy- $\alpha$ -naphthylamines, as well as the trihydroxynaphthalenes obtained from these by replacement of the amino-groups by hydrogen, are unknown.

*Benzeneazotrihydroxynaphthalene*,  $C_{16}H_{12}O_3N_2$ , forms slender, golden-brown crystals, m. p.  $186-188^{\circ}$ , dissolves in alkali hydroxide solution giving a deep blue, and in concentrated sulphuric acid giving an intense violet, coloration, and is not decomposed when boiled with dilute sulphuric acid for some hours. Its *tri-methyl ether*,  $C_{16}H_4(OMe)_3N_2Ph$ , forms slender, chestnut-coloured needles, m. p.  $145-146^{\circ}$ , and yields a *hydrochloride* and a *nitrate* crystallising in minute needles showing green, metallic reflection.

T. H. P.

**Azo-dyes from 5- and 8-Nitro- $\alpha$ -naphthylamines.** GILBERT T. MORGAN and FRANK RAYMOND JONES (*J. Soc. Chem. Ind.*, 1923, 42, 341—343T).—The formation of tarry impurities in the nitration of  $\alpha$ -naphthylamine to a mixture of 5- and 8-nitro- $\alpha$ -naphthylamines can be avoided by nitrating at a low temperature, between  $-9^{\circ}$  and  $-1^{\circ}$ , in concentrated sulphuric acid, and maintaining very vigorous stirring during addition of the nitrating acid to the sulphuric acid solution of  $\alpha$ -naphthylamine. A separation of the two products is effected through the sparing solubility of 5-nitro- $\alpha$ -naphthylamine sulphate in *N.* to 3*N.* sulphuric acid. Both 5- and 8-nitro- $\alpha$ -naphthylamines can be employed as primary, middle, and end components in the production of azo-dyes, and

the shades of colour obtained differ appreciably from those obtained with  $\alpha$ -naphthylamine.

3'-Sulphobenzene-4-azo-8-nitro- $\alpha$ -naphthylamine, obtained by coupling diazotised metanilic acid with 8-nitro- $\alpha$ -naphthylamine, forms a dark, brownish-red sodium salt and gives a dark crimson coloration with concentrated sulphuric acid. This dye and also 6':8'-disulphonaphthalene-2'(4)-azo-5-nitro- $\alpha$ -naphthylamine dye wool brownish-red. Toluene-p-4-azo-5-nitro- $\alpha$ -naphthylamine forms coppery brown four-sided prisms, m. p. 174–176°, giving an orange-red sulphuric acid coloration; its hydrochloride forms green, microscopic rhombohedra, m. p. 231°. It can be diazotised and coupled with resorcinol to give a diazo-dye. Diazotised 5-nitro- $\alpha$ -naphthylamine couples with chromotrope acid to form 5'-nitronaphthalene-1'(2)-azo-1:8-dihydroxynaphthalene-3:6-disulphonic acid, which dyes wool dark violet-red, changing to purple-black with chromium fluoride or copper sulphate; the sulphuric acid coloration is deep Prussian blue. The corresponding dye from 8-nitro- $\alpha$ -naphthylamine is similar but more soluble. The dye from diazotised 8-nitro- $\alpha$ -naphthylamine and acetyl-J acid (2-acetylamino-5-hydroxynaphthalene-7-sulphonic acid), coupled in alkaline solution, is sparingly soluble in the form of the free acid; it dyes wool brownish-scarlet and gives a brilliant blue coloration with sulphuric acid. The corresponding dye from 5-nitro- $\alpha$ -naphthylamine is almost insoluble in the form of the free acid; the sulphuric acid coloration is crimson-violet. Benzoyl-J acid appears to give two distinct products when coupled with 5- or 8-nitrodiazonaphthalene. The two diazo-compounds can also be coupled with  $\beta$ -naphthol on cotton fibre.

E. H. R.

**Diazo-ethers.** A. ANGELI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 539–543).—The views of Hantzsch and Reddelien ("Die Diazoverbindungen," 1921, 57) on the constitution of the few known diazo-ethers are discussed. The results obtained by the author during recent years show that azoxy-compounds contain, not the ring suggested by Kekulé,  $\begin{smallmatrix} \text{N} & \text{---} & \text{N} \\ & \diagdown & / \\ & \text{O} & \end{smallmatrix}$ , but the chain,  $\text{NO}\cdot\text{N}\cdot$ , and that, in the form of salts, nitroamines exhibit the structure  $\text{NR}\cdot\text{N}(\text{OH})\cdot\text{O}$ , and isonitroamines,  $\text{O}\cdot\text{NR}\cdot\text{N}\cdot\text{OH}$ . Moreover, the results of Angeli, Alessandri, and Aiazzi-Mancini (A., 1911, i, 544) show that the *N*-alkyl ethers of the oximes contain the grouping  $\text{C}\cdot\text{NR}\cdot\text{O}$ , which agrees fully with their mode of formation and with their behaviour, and also justifies the physical analogies between these compounds and the azoxy-compounds.

The possible structural isomerides of an aromatic diazo-hydroxide are (1)  $\text{NR}\cdot\text{N}\cdot\text{OH}$ , (2)  $\text{O}\cdot\text{NR}\cdot\text{NH}$ , (3)  $\text{NR}\cdot\text{NH}\cdot\text{O}$ , and (4)  $\text{NHR}\cdot\text{NO}$ . Replacement of the hydrogen atom may thus lead to ethers of four different types, compounds corresponding with each of these being known.

T. H. P.

**The Partial Decomposition of Proteins.** EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 129, 106–110; cf. this vol., i, 718).—Goose feathers when hydrolysed with sulphuric acid in  $\text{o}^{\circ}$ \*

the cold yield in addition to the substance previously described containing proline (3 mols.) and glycine (1 mol.), a substance,  $C_7H_{12}O_5N_2$ , m. p.  $251^\circ$  (decomp.),  $[\alpha]_D^{25} -136.0^\circ$  (5% solution in 5% sodium hydroxide solution). When this is hydrolysed, glycine, proline, and hydroxyproline are obtained, and it is concluded that this product consists of 1 mol. of glycine, 2 mols. of proline, and 1 mol. of hydroxyproline.

W. O. K.

**The so-called Artificial Globulin.** G. FANCONI (*Biochem. Z.*, 1923, 139, 321—335).—Albumin solutions from horse-serum were treated by two methods similar to those employed by Moll (*A.*, 1904, i, 356) and Ruppel, by which they claimed to convert the albumin into globulin. The solutions developed the ammonium sulphate precipitation reactions of a globulin, but neither of the "artificial globulin" preparations agreed in all their physical properties with the natural globulin obtained from the same serum. The two preparations were not identical, and they did not show the antigen properties of natural serum-globulin. Moll's preparation in this respect resembled the parent albumin, whilst the other was inactive and behaved like a racemised protein. It is concluded that no evidence exists for the transformation of albumin into globulin in vitro.

J. P.

**The Purification and Precipitation of Casein.** JOHN H. NORTHBOP (*J. Gen. Physiol.*, 1923, 5, 749—750).—Purified casein is conveniently prepared by precipitating the casein from milk as described by L. Van Slyke and Baker (*A.*, 1918, i, 413), and then washing thoroughly to remove salts. Ten g. are then suspended in 1 litre of water, and the suspension brought to a  $p_H$  of from 2.5 to 3 by the addition of hydrochloric acid. The cloudy solution is filtered and a solution of sodium hydroxide added until the  $p_H$  is 4.7. The precipitate is then washed with distilled water. This method avoids the denaturation by acid, which very easily occurs if the casein is dissolved in alkali and reprecipitated by acid.

W. O. K.

**The Constitution of Proteins. The Structure of Silk Fibroin.** EMIL ABDERHALDEN and WALTER STIX (*Z. physiol. Chem.*, 1923, 129, 143—156).—Chlorodinitrobenzene in presence of sodium hydrogen carbonate reacts with a free amino-group of an amino-acid to yield dinitrophenylamino-derivatives. It will not react with the  $-NHCO-$  grouping in a simple straight chain but reacts with a diketopiperazine ring. More chlorodinitrobenzene is found to combine with silk fibroin than corresponds with the number of free amino-groups. This may be explained by the existence in the protein molecule of diketopiperazine groups.

The following new compounds have been prepared. *Ethyl  $\alpha$ -dinitrophenylaminopropionate*, yellow crystals, m. p.  $60^\circ$ . *Dinitrophenyltyrosine*, m. p.  $57^\circ$ . *Dinitrophenyltyrosine ethyl ester*, a yellow, amorphous compound, m. p.  $46^\circ$ . *Dinitrophenylacetyltyrosine*, m. p.  $106^\circ$ .  *$\alpha$ -Dinitrophenylamino- $\beta$ -dinitrophenylglyoxypropionic acid*, from 1 mol. of tyrosine and 2 mols. of chlorodinitrobenzene, m. p.  $84^\circ$ . *Dinitrophenyl-leucylglycine*, yellow crystals,

m. p. 120°. *Di(chloromononitrobenzyl)leucylglycine anhydride*, m. p. 75–76°, from the condensation of dinitrochlorobenzene and leucylglycine anhydride. Apparently, a loss of nitro-groups occurs.

W. O. K.

**Formoxyhæmin.** WILLIAM KÜSTER and ERHARD WILLIG (*Z. physiol. Chem.*, 1923, **129**, 130–142).—If washed coagulated blood is extracted with methyl alcohol containing sulphuric acid, and the extract boiled with the addition of formic acid,  $\beta$ -formoxymonomethylhæmin is obtained. Extraction with methyl alcohol containing formic acid yields  $\alpha$ -formoxymethylhæmin, described by Partos (cf. A., 1922, i, 596).  $\beta$ -Formoxymethylhæmin is distinguished from the  $\alpha$ -form by its solubility in hot sodium carbonate solution. It forms a bluish-black powder, leaflets, prisms, and rhombs, with the formula  $C_{35}H_{34}O_4N_4FeO\cdot CHO$ . Two forms of formoxyhæmin have also been obtained. By extracting coagulated blood with acetone containing formic acid, the  $\alpha$ -form is obtained, needles, insoluble in sodium hydrogen carbonate solution, of the formula  $C_{34}H_{32}O_4N_4FeO\cdot CHO$ . This is methylated with difficulty with diazomethane to yield a monomethyl derivative which could not be obtained crystalline, but may be identical with Partos's compound. If the coagulated blood is extracted with acetone containing sulphuric acid and the filtrate heated with formic acid and sodium formate, a  $\beta$ -formoxyhæmin, fine needles, is obtained soluble in sodium carbonate solution and easily methylated with diazomethane to yield a monomethyl derivative. If in the preparation of  $\beta$ -formoxyhæmin, acetone containing methyl alcohol is used, a  $\beta$ -formoxymonomethylhæmin is obtained. It is suggested that the  $\alpha$ -form of the hæmin group is present in hæmoglobin, and that if a strong mineral acid (sulphuric acid) is used in the extraction the attachment of one of the carboxyl groups to the iron atom is loosened, and a derivative of the  $\beta$ -type is obtained.

W. O. K.

**Thiocyanohæmins.** WILLIAM KÜSTER (*Z. physiol. Chem.*, 1923, **129**, 157–187).—Thiocyanohæmin may be obtained in two forms analogous to the  $\alpha$ - and  $\beta$ -forms of chlorohæmin or of formoxyhæmin.  $\alpha$ -Thiocyanohæmin,  $C_{34}H_{32}O_4N_4Fe\cdot SCN$ , is formed when defibrinated blood is added to acetic acid containing thiocyanic acid. It may be recrystallised as dark brown prisms or rods, or six-sided leaflets, from a mixture of pyridine and chloroform if it is not allowed to remain too long in contact with the solvent. It is insoluble in 5% sodium hydrogen carbonate solution, is methylated by diazomethane only with difficulty and incompletely, and shows a rather low conductivity in benzonitrile solution. If the crude  $\alpha$ -thiocyanohæmin is allowed to remain in contact with the chloroform-pyridine mixture for two days, a *pseudo*- $\beta$ -thiocyanohæmin, six-sided leaflets, is formed. This is soluble in 5% sodium hydrogen carbonate solution, and in methyl alcohol containing sulphuric acid, but not in pure methyl alcohol, and its solution in benzonitrile possesses a higher conductivity than that of  $\alpha$ -thiocyanohæmin. One carboxyl group may be

completely methylated and the other partly. If  $\alpha$ -thiocyanohæmin is allowed to remain in contact with the chloroform-pyridine mixture for two hours, the product consists chiefly of  $\beta$ -thiocyanohæmin. This compound may be conveniently prepared following Zaleski's method. The blood-coagulum is extracted with acetone containing sulphuric acid, and to the extract is added ammonium thiocyanate. Crystals of (acetone)- $\beta$ -thiocyanohæmin separate, and when recrystallised from a mixture of acetone and pyridine this compound forms deep bluish-black prisms with a metallic lustre, of the formula  $C_{35}H_{33}O_4N_4Fe\cdot SCN$ . It is slowly soluble in 5% sodium hydrogen carbonate solution at room temperature. Thiocyanic acid is split off only with difficulty by alkali, and only very slightly by pyridine, whereas  $\beta$ -chlorohæmin is very easily decomposed by these reagents. Diazomethane forms from  $\beta$ -thiocyanohæmin a mixture of (acetone)-dimethyl- $\beta$ -thiocyanohæmin, obtusely pointed prisms stable towards 5% sodium carbonate solution even on heating, and (acetone)monomethyl- $\beta$ -thiocyanohæmin. Monomethyl- $\beta$ -thiocyanohæmin may be prepared, following Mörner, by extracting blood coagulum with methyl alcohol containing sulphuric acid, and precipitating the extract with ammonium thiocyanate. It forms needles,  $C_{35}H_{34}O_4N_4Fe\cdot SCN$ , soluble in hot sodium carbonate. If blood coagulum be extracted with acetone containing sulphuric acid, a 5% solution of thiocyanic acid saturated with ammonium thiocyanate added, and the mixture boiled for thirty minutes, a pseudo- $\beta$ -(acetone)thiocyanohæmin is obtained, forming prisms, soluble in sodium hydrogen carbonate solution and in acid methyl alcohol, which may be partly methylated by diazomethane. Chlorohæmin may be converted into a pseudo- $\beta$ -thiocyanohæmin by dissolving in a mixture of chloroform and acetone and treating the solution with 5% thiocyanic acid saturated with ammonium thiocyanate. Measurements of the conductivity of various hæmin derivatives in pyridine and benzonitrile are given.

W. O. K.

**The Isolation of Nucleic Acid from Tissues.** WALTER JONES and CASPAR FOLKOFF (*Bull. Johns Hopkins Hosp.*, 1922, **33**, 443—444).—The method of isolation of the additive product of yeast-nucleic acid with ammonium acetate is described in detail. The crude acid, after having been separated, is ground with ammonium hydroxide solution, the excess of which is not neutralised until after the addition of alcohol. Subsequent addition of alcohol yields a pure product. The procedure described cannot be employed in the case of animal glands. CHEMICAL ABSTRACTS.

**The Course of Enzyme Reactions.** SVANTE ARRHENIUS (*Z. angew. Chem.*, 1923, **36**, 455—456).—The most completely investigated enzyme reactions are non-molecular, i.e., the quantity of substrate converted is proportional to the time. Exceptions to this simple law, which depends on the substrate being in large excess of the enzyme, occur when this condition is not realised, when the enzyme becomes decomposed, and when the reaction products enter into the reaction.

H. C. R.

**The Inactivation of Trypsin. IV. The Adsorption of Trypsin by Charcoal.** JOHN H. NORTHEOP (*J. Gen. Physiol.*, 1923, 5, 751—755).—The removal of trypsin from solution by charcoal is not reversible, and is independent of the  $p_H$  over a wide range ( $p_H$  3 to  $p_H$  9). Charcoal previously treated with gelatin does not remove trypsin from solution. These facts demonstrate that the inactivation of trypsin by charcoal is essentially different from the inactivation by serum, which is a homogeneous reaction (cf. this vol., i, 261). W. O. K.

**The Specificity of Enzymes. V. Comparison of Yeast- and Taka-saccharase.** RICHARD KUHN (*Z. physiol. Chem.*, 1923, 129, 57—63).—The inversion of saccharose by yeast-saccharase is not inhibited by  $\alpha$ -glucose, whilst it is strongly inhibited by  $\beta$ -glucose or by levulose. On the other hand, the action of taka-saccharase is retarded strongly by  $\alpha$ -glucose and not by  $\beta$ -glucose or by levulose. Inversion by fresh yeast-cells in presence of toluene is also not inhibited by  $\alpha$ -glucose. W. O. K.

**The Action of Halogens on Diastases.** L. BERCELLER and J. FREUD (*Biochem. Z.*, 1923, 139, 476—481).—As in the case of ptyalin (this vol., i, 404), it is now shown that the action of malt diastase on starch is also decreased by iodine. The presence of starch has a protective effect on the enzyme against iodine inactivation. Bromine and chlorine also inactivate both ptyalin and malt diastase, and again the presence of starch protects these from the halogens. Bromine and chlorine do not inhibit the acid hydrolysis of starch as does iodine. J. P.

**Effect of Amino-acids in Retarding the Hydrolytic Decomposition of an Enzyme (Pancreatic Amylase).** H. C. SHEERMAN and FLORENCE WALKER (*J. Amer. Chem. Soc.*, 1923, 45, 1960—1964).—Highly purified preparations of pancreatic amylase, which deteriorate more rapidly in aqueous solution than the other amylases studied (*A.*, 1920, i, 101; 1922, i, 283) are also more affected by the presence of amino-acids (*loc. cit.*). In the following experiments, the activity of the amylase is measured by the amount of reducing sugar (chiefly maltose) formed when the quantity of enzyme necessary to saccharify about one-fifth of the substrate acts for thirty minutes at 40° on 100 c.c. of a 10% dispersion of Lintner "soluble" starch, the reducing sugar being subsequently estimated by means of Fehling's solution. Solutions of pancreatic amylase containing optimum concentrations of sodium chloride and disodium hydrogen phosphate which have been kept for one hour at 40° show considerably greater activity when alanine has been added to the solution previously. Amylase solutions to which the salts have not been added deteriorate more rapidly, and with these the protective action of the amino-acid may be demonstrated at 22°. There is a striking increase, between 30° and 60°, in the apparent activation by means of glycine or phenyl-alanine with increasing temperature of digestion, but above about 60° coagulation of the enzyme occurs, this not being prevented by the presence of the amino-acids. At the same temperatures, using

half the amount of enzyme solution but allowing the reaction to proceed twice as long, the apparent activation is even greater.

All these facts indicate that the favourable influence of amino-acids on the enzymic hydrolysis of starch is due largely, or perhaps even entirely, to a protection of the enzyme from deterioration (probably gradual hydrolytic decomposition) in the aqueous dispersion in which it acts. This is thought to support the view that the enzyme itself is of protein nature, or contains protein as an essential constituent.

W. S. N.

**The Specificity of Enzymes. IV. The Simple Nature of the  $\beta$ -Glucosidase of Emulsin.** RICHARD WILLSTÄTTER, RICHARD KUHN, and HARRY SOBOTKA (*Z. physiol. Chem.*, 1923, 129, 33—56).—It has been found that the ratios of the time-values for  $\beta$ -glucosidase acting on helicin, salicin,  $\beta$ -phenylglucoside, arbutin, and  $\beta$ -methylglucoside do not remain constant (cf. A., 1922, i, 390). It does not, however, follow that the different glucosides are hydrolysed by different enzymes. The affinity constant  $K = (\text{Free Enzyme}) \times (\text{Substrate}) / (\text{Enzyme-Substrate})$  varies with different preparations. When correction is made for this varying affinity it is found that the ratio of the activities of the enzyme preparations acting, for example, on salicin and  $\beta$ -methylglucoside, remains approximately constant. The variations, therefore of the time-value ratios are not to be referred to variations in the active groups, but rather to the variations in the affinities, no doubt depending on the colloids present in the different preparations.

W. O. K.

**The Influence of Glycine on the Fermentative Action of a Soja-bean Urease. II. The Stable Constituent of Soja-bean Urease.** NAOSABURO KATÔ (*Biochem. Z.*, 1923, 139, 352—365).—In a previous communication (this vol., i, 622) the author postulated the presence of two constituents in urease. This has now been confirmed. The urease system consists of a thermolabile constituent which possesses fermentative properties, and a thermo-stable constituent with no fermentation action, which the author calls "Stable Component X." This last, at carbamide concentrations above the "equivalent carbamide concentration" (*loc. cit.*), increases the activity of the urease, but has no influence at substrate concentrations below this value, thus resembling in its action the effect of the addition of glycine to urease. The action of "Stable Component X" is not due to a  $p_H$  effect or to the presence of mineral salts.

J. P.

**Researches on Antimony. I. Tri-*m*-xylylstibine and its Derivatives.** ARCHIBALD EDWIN GODDARD (*T.*, 1923, 123, 2315—2323).

**Preparation of Alkyl Compounds of Boron.** ERICH KRAUSE (D.R.-P. 371467; from *Chem. Zentr.*, 1923, ii, 1089; cf. A., 1922, i, 22, 604).—Boron trifluoride is allowed to react with organo-magnesium halides. The following compounds are mentioned: boron phenyl difluoride,  $BPhF_2$ , an oil, b. p. 70—75°; boron *p*-tolyl

*disfluoride*, an oil, b. p. 95—97°; *phenylboric acid*, needles, m. p. 218°; *p-tolylboric acid*, needles, m. p. 240°; *p-chlorophenylboric acid* (from magnesium *p*-chlorophenyl bromide and boron trifluoride), sheafs of needles, m. p. 275°; *p-bromophenylboric acid*, needles, m. p. 191°; *benzylboric acid*, crystals, m. p. 161°.

G. W. R.

### Physiological Chemistry.

**Influence of the Medium of the Respiration of Living Cells.** W. RYFFEL (*Z. physiol. Chem.*, 1923, 125, 223—247).—The respiratory activity of the living cell measured by the reduction of *m*-dinitrobenzene to *m*-nitrophenylhydroxylamine is greatest at a concentration of  $\text{PO}_4'''$  of 0.08—0.09 M., at  $p_{\text{H}}$  9—10, and at a temperature, in the case of guinea-pigs and pigeons, of about 40°, and of frogs of between 20° and 35°.

W. O. K.

**The Effects on the Circulation and Respiration of an Increase in the Carbon Dioxide Content of the Blood in Man.** E. C. SCHNEIDER and DOROTHY TRUESDELL (*Amer. J. Physiol.*, 1922, 63, 155—175).—Among the physiological effects observed on gradual increase of the amount of carbon dioxide in inspired air were an increased pulse rate; increased arterial, capillary, and venous blood pressures; increased minimum volume and frequency of breathing.

CHEMICAL ABSTRACTS.

**The Respiratory Exchange and Blood-sugar Curves of Normal and Diabetic Subjects after Epinephrine [Adrenaline] and Insulin.** RICHARD S. LYMAN, ELIZABETH NICHOLLS, and WM. S. McCANN (*J. Pharm. Expt. Ther.*, 1923, 21, 343—365).—Investigations are described on the effect of administration of adrenaline and of insulin on the respiratory quotient, heat production, blood-sugar, pulse rate, and blood pressure of normal and of diabetic patients. Adrenaline was found as usual to increase the respiratory quotient, heat production and the blood-sugar, whilst insulin increased the respiratory quotient and the heat production but diminished the blood-sugar. Insulin and adrenaline, when injected together, have, generally speaking, an additive effect.

W. O. K.

**The Effect of Parasympathetic Stimulation, especially by Means of Choline, on the Blood-sugar.** K. DRESEL and H. ZEMMIN (*Biochem. Z.*, 1923, 139, 463—469).—The subcutaneous and oral administration of choline to normal and diabetic subjects produced a diminution in blood-sugar, minimal values being reached in from one-half to two hours in the former, and in from two to four hours in the latter method of administration. This is ascribed to parasympathetic stimulation. The results of Bornstein and Vogel (*A.*, 1922, i, 80), who observed an increase of blood-

sugar on parasympathetic stimulation using pilocarpine and physostigmine, are ascribed to the unsuitability of the stimulants.

J. P.

**The Reversibility of Fibrin Coagulation. II.** G. BARRAN and ADALBERT GASPÄR (*Biochem. Z.*, 1923, 139, 291—301).—Fibrin obtained from untreated blood plasma, in contrast to that obtained from oxalated or fluoride plasma, has no tendency to dissolve in 0.02% sodium hydroxide. If the insoluble fibrin be subsequently treated with 0.2% sodium oxalate or 0.75% sodium fluoride, it becomes, in part, soluble in dilute alkali. These results, in conjunction with the authors' previous work (*Biochem. Z.*, 1923, 136, 411), are regarded as opposing the view that fibrin coagulation is reversible.

J. P.

**Effect of Coagulation on the Amino-nitrogen Content of Blood.** F. PETITJEAN (*Compt. rend. Soc. Biol.*, 1923, 87, 1001—1004; from *Chem. Zentr.*, 1923, i, 1464—1465).—In the coagulation of blood a small initial decrease in the amino-nitrogen content is followed by an increase. The content after complete coagulation almost approximates to the original amino-nitrogen content. In certain cases, an increase is observed.

G. W. R.

**Amino-acids of the Blood. I. Behaviour during Digestion. II. On Prolonged Fasting.** S. MARINO (*Arch. Farm. speriment. Sci. aff.*, 1923, 36, 20—32, 56—64).—I. The defibrinated blood of a fasting dog is found to contain from 3.3 to 6.6 mg. of amino-acids per 100 c.c. When proteins are undergoing digestion, the blood sometimes contains less than the normal proportion of amino-acids, but in other cases shows almost double the proportion present during fasting. In general the content tends to resume its normal value after the digestion of protein has proceeded for six hours.

II. If fasting is prolonged to the death of the animal, the blood exhibits a considerable increase in amino-acid content, although different animals show marked variations in this respect. Such increase, which is manifested almost exclusively after the twelfth day of fasting, is subsequently progressive until death ensues. In the latter stage, the proteins are probably hydrolysed so rapidly that the resulting amino-acids cannot be utilised and consequently accumulate in the blood; this effect may be aggravated by the pronounced autolytic changes and by the inefficiency of the regulating mechanism.

T. H. P.

**The Blood of Mother and Fœtus.** M. G. HOWE and M. H. GIVENS (*Amer. J. Diseases Children*, 1923, 25, 63—75).—The non-protein nitrogen and urea-nitrogen in maternal blood at parturition are normal. The values vary but there is no consistent preponderance in either blood. Differences are attributed to maternal or foetal renal insufficiency or impairment of placenta. The concentration of blood uric acid of parturient women tends to be higher than normal. The concentration of blood-sugar is temporarily increased at parturition, maternal values being greater

than foetal. This is due to the anæsthetic, to muscular contractions, and possibly to a psychic factor.

CHEMICAL ABSTRACTS.

**The Distribution of Urea in Human Blood and in Secretions.** J. BERNARD COHEN (*Biochem. Z.*, 1923, 139, 516—526).—Using the urease method and estimating the evolved ammonia in a micro-Kjeldahl apparatus, urea determinations were made on whole human blood and on plasma. In twelve recorded normal cases only three showed an equilibrium distribution of urea between corpuscles and plasma. In the other cases, the ratio corpuscle urea: plasma urea varied from 0.5 to 2.1. Similar results were obtained in eight cases of uræmia, and these were confirmed in dogs with high blood ureas produced by ligation of the pancreatic duct. Human bile, duodenal juice, and cerebrospinal fluid all contain less urea than the corresponding blood, and in the case of bile the urea content is higher during fasting than when food is being taken.

J. P.

**The Origin of the Lipase in Blood.** KEIZO HIRUMA (*Biochem. Z.*, 1923, 139, 336—341).—Ligation of the pancreatic duct in dogs caused an increase of lipase in the blood, the maximum increase being reached after four days. In eight to nine days the lipase content had returned to normal, due to the lessened activity of the secreting cells following on the ligation. No lipase appeared in the urine. Blood-serum collected from the pancreatico-duodenal vein contained more lipase than that from the portal vein, which in turn showed a higher content than that from the femoral artery and vein. These observations are taken to indicate the pancreas and intestine as the seat of origin of blood lipase, but this view does not accord with the results of Rona and Pavlovic (this vol., i, 403) on the action of quinine and atoxyl on various lipases.

J. P.

**Antihæmolytic Effect of Antithrombin.** NICOLAS L. COSMOVICI (*Compt. rend. Soc. Biol.*, 1923, 88, 538—540; from *Chem. Zentr.*, 1923, i, 1520).—Antithrombin from the serum of rabbits was found to exert an antihæmolytic effect on a mixture composed of sheep blood-corpuscles and guinea-pig complement in sodium chloride solution. The effect is intensified by the alkalinity of the liquid containing the antithrombin.

G. W. R.

**The Cholesterol Balance.** S. J. THANNHAUSER (*Deut. arch. Klin. Med.*, 1923, 141, 290—311; from *Chem. Zentr.*, 1923, i, 1403—1404).—[With W. FLEISCHMANN.]—An enzyme which hydrolyses cholesterol esters was shown to be present in duodenal juice, pancreatic solution, and bile.

[With E. ANDERSEN.]—Cholesterol is estimated in total blood and in serum by the gravimetric method of Windaus after addition of anhydrous calcium sulphate and ether.

[With ECARIUS.]—The equilibrium between free cholesterol and cholesterol in the form of esters is held to be due to the function

of organs, in particular, the liver, and not to a specific enzyme in the blood.

[With PAUL VON MILLER, H. SCHABER, and C. MONCORPS].—Experiments are described on the cholesterol balance with diets low in cholesterol and fat.  
G. W. R.

**Tetany. I. The Effect of Calcium Chloride Ingestion on the Acid-Base Metabolism of Infants.** J. L. GAMBLE, G. S. ROSS, and F. F. TISDALL (*Amer. J. Diseases Children*, 1923, 25, 455—469).—Ingested calcium chloride behaves as an acid substance since the concentration of the chloride-ion absorbed is greater than that of the calcium-ion. The effect on acid-base metabolism of the ingestion of 1 g. of calcium chloride is equivalent to that of the ingestion of milk containing 75 c.c. of 0.1N-hydrochloric acid. This increase in acid over fixed alkali claiming excretion in the urine is compensated by an increase in urinary acidity and ammonia excretion resulting in a normal base concentration of blood plasma. The lowering of hydrogen carbonate following calcium chloride ingestion is due to a rise in chloride-ion concentration displacing an equivalent amount of bound carbon dioxide. Excretion of fixed alkali, especially of sodium and potassium in the urine, is increased following ingestion of calcium chloride, in consequence of a reduction in the volume of body-water rather than by actual withdrawal of base from body fluids.  
CHEMICAL ABSTRACTS.

**Tetany. II. The Effect of Ingestion of Hydrochloric Acid-producing Substances on the Acid-Base Metabolism of an Infant and the probable manner of their Action in the Treatment of Tetany.** J. L. GAMBLE and G. S. ROSS (*Amer. J. Diseases Children*, 1923, 25, 470—497).—Plasma bicarbonate is lowered following the administration of calcium chloride, ammonium chloride, and hydrogen chloride to an infant with tetany, in consequence of an increased metabolism of hydrogen chloride which produces an abnormally high chloride-ion content of the plasma at the expense of bicarbonate; the total base of the plasma remains stationary. The hydrogen-ion concentration of the plasma is considerably increased. The metabolism of these substances leads to an increased excretion of phosphates and of fixed alkali in the urine in consequence of a reduction of the volume of body-water due to diuresis. Ammonium chloride does not raise the lowered calcium content of the plasma found in tetany, its therapeutic action being ascribed to the production of an increased ionisation of calcium; calcium chloride and hydrogen chloride, however, cause in addition an increase in the calcium content of the plasma.  
CHEMICAL ABSTRACTS.

**Retention of Bismuth by the Brain.** P. LEMAY and L. JALOUSTRE (*Compt. rend. Soc. Biol.*, 1923, 88, 474; from *Chem. Zentr.*, 1923, i, 1517).—Comparatively large amounts of bismuth were found in the brains of two individuals to whom bismuth hydroxide had been administered.  
G. W. R.

### The Metabolism of Phosphorus of the Nervous System.

II. Phosphorus Content under Various Conditions. ELISABETH HECKER (*Z. physiol. Chem.*, 1923, 129, 26—32).—The phosphorus content of the surviving central nervous system of the frog kept in isotonic sodium chloride solution and supplied with oxygen shows a decrease of about 15—16%. This decrease occurs almost entirely during the first eight hours. This loss of phosphorus is decreased by the application of a narcotic such as urethane, and is increased by electrical excitation, and there is no decrease if oxygen is excluded.

W. O. K.

### The Metabolism of Phosphorus of the Nervous System.

III. The Phosphorus-sparing Substances in the Metabolism of the Central Nervous Organs. ELISABETH HECKER (*Z. physiol. Chem.*, 1923, 129, 205—219).—At rest or under stimulation the phosphorus content of the central nervous system decreases, but the presence of galactose, levulose, or of cerebrin reduces this loss. In the presence of brain lecithin, there is practically no loss. Neutral phosphate solutions also cause a decrease of the loss of phosphorus, but the best effect is obtained by a combination of phosphates and brain lecithin. The temperature influences the magnitude of the changes and so also, in the case of the stimulated preparation, does the strength of the stimulation.

W. O. K.

### The Metabolism of Phosphorus of the Nervous System.

IV. The Phosphorus Metabolism of the Peripheral Nerves. ELISABETH HECKER (*Z. physiol. Chem.*, 1923, 129, 220—222).—A nerve (ischiodicus) of the frog contains about 0.2% of phosphorus (calculated on the fresh substance). No change in the phosphorus content could be detected in the resting nerve, but under stimulation it decreased by about 10% in eight hours.

W. O. K.

The Free Sugar Content of the Liver and its Relation to Glycogen Synthesis and Glycogenolysis. CARL F. CORI, G. T. CORI, and G. W. PUCHER (*J. Pharm. Expt. Ther.*, 1923, 21, 377—389).—Under normal conditions, glycogen is synthesised in the liver when the free liver-sugar is high, but if insulin is administered, glycogen synthesis takes place at a much lower level of liver-sugar. Adrenaline causes glycogenolysis and the free liver-sugar is increased.

W. O. K.

The Biological Decomposition of Uric Acid. H. STEUDEL and S. IZUMI (*Z. physiol. Chem.*, 1923, 129, 188—194).—An extract prepared from finely divided ox-kidneys, which in the presence of oxygen converted uric acid into allantoin, was unable to form allantoin from uroxylic acid,  $(\text{NH}_2\cdot\text{CO}\cdot\text{NH})_2\text{C}(\text{CO}_2\text{H})_2$ .

W. O. K.

Composition of a Cystic Liquid. E. MAURIN (*Ann. Chim. Analyt.*, 1923, [ii], 5, 207—208).—A scrotal cyst yielded 155 c.c. of a slightly turbid, pink liquid,  $d$  1.007. The liquid contained: total solids, 1.235%; ash, 1.062%; serine, 0.135%; globulin, 0.015%; nuclealbumin, trace; peptone, none; pseudomucin, none; urea, 0.075%; dextrose, none; cholesterol, trace; chlorides (as NaCl), 0.012%; phosphates (as  $\text{P}_2\text{O}_5$ ), 0.020%.

W. P. S.

**Composition of Cyst Fluid (of Cattle).** P. MAZZOCCO (*Compt. rend. Soc. Biol.*, 1923, 88, 342—343; from *Chem. Zentr.*, 1923, i, 1334).—The colourless, transparent cyst fluid from cattle rarely becomes turbid on being heated. It has  $d$  1.006—1.009. The reaction is alkaline to litmus, acid to phenolphthalein in the cold, and alkaline on warming. The total alkalinity to sulphuric acid is 0.010—0.018%. The composition is as follows:  $\text{Na}_2\text{O}$ , 0.53%;  $\text{K}_2\text{O}$ , 0.04—0.05%;  $\text{CaO}$ , 0.005—0.006%;  $\text{Fe}$ , trace;  $\text{MgO}$ , 0.005—0.007%;  $\text{NaCl}$ , 0.668—0.700%;  $\text{SO}_3$ , 0.35—0.43%;  $\text{P}_2\text{O}_5$ , 0.026—0.030%;  $\text{SiO}_2$ , trace; dextrose, 0.03—0.4%; glycogen, trace; total fatty acids, 0.036—0.041%; unsaponifiable acids, 0.01—0.015%; cholesterol, 0.003—0.004%; proteins, 0.09—0.15%; total nitrogen, 0.069—0.080%; non-protein nitrogen, 0.034—0.040%; carbamide nitrogen, 0.025—0.028%; amino-acids, 0.025—0.028%; histidine, 0.0024—0.010%. The blood of the same animals contains twice as much dextrose and approximately the same amount of carbamide nitrogen and non-protein nitrogen.

G. W. R.

**The Influence of Various Antipyretics on the Distribution of Nitrogen in the Urine.** KIYOSHI MORINAKA (*Z. physiol. Chem.*, 1923, 129, 111—129).—The effect of antipyretics on the various fractions of the nitrogen content of urine (rabbit, dog, and man) varies according to the particular drug used. Some, such as antifebrin, have little influence; others, such as elbon or phenacetin, cause amongst other effects, increased amino-acid nitrogen, probably to be associated with increased protein decomposition. The drugs investigated were elbon (cinnamoylhydroxyphenylcarbamide), phenacetin, sodium salicylate, aspirin, quinine, remigin (ethylhydrocupreine), antipyrine, pyramidone, and antifebrin.

W. O. K.

**Distribution and Elimination of Organic Arsenic Compounds after Intravenous Administration.** F. M. R. BULMER (*J. Pharm. Expt. Ther.*, 1923, 21, 301—311).—After intravenous administration of salvarsan, arsenic first of all accumulates in the liver, but it disappears rapidly from that organ, being excreted in the bile, which seems to be the main route by which the organism eliminates arsenic. It also tends to accumulate in the lungs, where it remains for several days, whilst it is retained in the long bones for a longer period than in any of the other tissues analysed.

W. O. K.

**Penetration of Arsenic into the Cerebrospinal Fluid.** CARL VOEGTLIN, M. I. SMITH, HELEN DYER, and J. W. THOMPSON (*U.S. Public Health Repts.*, 1923, 38, 1003—1021).—The penetration of arsenic into the cerebrospinal fluid, following the intravenous injection of a variety of arsenicals, has been studied by (a) the chemical analysis of the blood, brain, and cerebrospinal fluid for the presence of arsenic, and (b) the parasitocidal action obtainable in the cerebrospinal fluid. The distribution of arsenic in various tissues and body-fluids after injection of several preparations has also been studied. Normal rabbits fed on oats and kale contained 0.69 micro-mg. of arsenic per g. of cerebrospinal fluid. The brain of

normal animals contained an average of 0.02 micro-mg. arsenic per g. of fresh tissue. *Trypanosoma equiperdum* is killed in blood suspension in vitro by 7.5 micro-mg. of arsenic from "arsenoxide," in six minutes. Salvarsan, neo-salvarsan, and silver salvarsan have a relatively low effectiveness unless very large doses are used. Sulpharsphenamine is the most effective arsenobenzene derivative studied. A greater therapeutic effect can be expected from large single doses given at long intervals than from smaller doses administered more frequently. Sulpharsphenamine, tryparsamide, and 3-amino-4-hydroxyphenylarsinic acid are suggested as remedies of superior penetrative power.

CHEMICAL ABSTRACTS.

### Chemistry of Vegetable Physiology and Agriculture.

**The Importance of Sequence in Biology. III.** L. KARCZAG and K. HAJÓS (*Biochem. Z.*, 1923, 139, 345—351).—A continuation of the authors' work (A., 1922, i, 302) on the effect of varying the order of addition of the components of a reacting system. It is shown that, in the case of the Wassermann reaction, variations in (1) the sequence of addition of the components of the first phase (serum, antigen, complement, and salt) and (2) the order of addition of hæmolyisin and erythrocytes has, in both cases, a marked effect on the intensity of the reaction.

J. P.

**Butylene Glycol Fermentation of Dextrose by *Bacillus proteus*.** M. LEMOIGNE (*Compt. rend. Soc. Biol.*, 1923, 88, 467—468; from *Chem. Zentr.*, 1923, i, 1460).—The formation of butylene glycol by the action of three types of *Bacillus proteus* on substrates containing dextrose was shown by isolation of acetylmethylcarbinol and  $\beta$ -butylene glycol from the products of fermentation.

G. W. R.

**The Production of Carbon Dioxide and Volatile Acids by Propionic Bacteria, with special reference to their Action in Cheese.** J. M. SHERMAN and R. H. SHAW (*Sci. Proc. Amer. Soc. Bacteriologists, Abstracts Bact.*, 6, 16).—*Bacterium acidipropionici* (d) can produce carbon dioxide, propionic acid, and acetic acid from succinates, glycerol, peptone, and possibly to a slight degree from butter fat. In the case of succinates and glycerol, about twice as much propionic acid was produced as acetic acid; in the case of peptone, the amount of acetic acid was larger than in the other cases. Aspartic acid yielded only carbon dioxide and acetic acid.

CHEMICAL ABSTRACTS.

**Intermediate Products of the Bacterial Decomposition of Cellulose.** CARL NEUBERG and REINHOLD COHN (*Biochem. Z.*, 1923, 139, 527—549).—In the bacterial fermentation of cellulose at 37° with production of hydrogen and methane, and at 53° to 55° by thermophilic bacteria, acetaldehyde was detected as an intermediate product and isolated as the sulphite compound and in combination

with dimethylhydrosoreinol. Of the breakdown products of cellulose, cellobiose and dextrose underwent fermentation by the cellulose bacteria with formation of butyric acid, in the former case, and acetaldehyde in both, whilst Hess's anhydrobiose gave negative results. The anhydrobiose is susceptible to fermentation by cultures of *Bacillus butylicus*, which also ferments cellobiose but not cellulose. Acetaldehyde was detected during the butyric acid fermentation of anhydrobiose and cellobiose and, in the latter case, traces of dextrose were also found. It is concluded that the hydrogen and methane fermentation of cellulose proceeds like a butyric acid fermentation with the subsequent intermediate formation of acetaldehyde.

J. P.

\* **Digestion of Cellulose by the Intestinal Flora of Man.** *Bacillus cellulose dissolvens*, n.sp. (MME) Y. KHOUVINE (Ann. Inst. Pasteur, 1923, 37, 711—752).—A detailed account is given of the isolation from the human intestinal flora in 60% of the cases of an anaërobe, *Bacillus cellulose dissolvens*, n.sp. It is best cultivated in media containing faecal extractives. Its separation as a pure culture from other bacteria is difficult, but depends on its great resistance to heat, the terminal spore resisting boiling for 40—50 minutes and also saturated chloropicrin solution. It does not appear to act on sugars, but only on cellulose, which it digests, with formation of carbon dioxide, hydrogen, ethyl alcohol, acetic, butyric, and probably lactic acids. It disintegrates 1 g. of cellulose in sixteen days, but in the presence of other bacteria it can cope with five times as much cellulose. The paper is illustrated by photomicrographs which show, inter alia, the attachment of the bacilli to the cellulose fibres by their non-sporulating terminations. H. K.

**Micro-organisms Concerned in the Oxidation of Sulphur in the Soil. V. Bacteria Oxidising Sulphur under Acid and Alkaline Conditions.** S. A. WAKSMAN (*J. Bact.*, 1922, 7, 609—616).—In acid soils, *Thiobacillus thio-oxidans* rapidly oxidises sulphur, whilst *Thiobacillus-B*, which is commonly present in cultivated soils, is active in alkaline soils. CHEMICAL ABSTRACTS.

**Influence of Ultra-violet Light on Alcoholic Fermentation.** N. L. SÖHNGEN and C. COOLHAAS (*Woch. Brau.*, 1923, 40, 187—188).—Contrary to the results obtained by R. and R. de Fazi (*A.*, 1922, i, 1219), ultra-violet light from a quartz lamp is found to exert a harmful influence both on the fermenting and on the reproductive capacity of yeast, unless the distance of the lamp from the solution is large and the time of illumination short, in which case no effect at all is noticeable.

W. T. K. B.

**Auto-fermentation of Yeast.** H. VON EULER and KARL MYRÅCK (*Z. physiol. Chem.*, 1923, 129, 195—204).—The auto-fermentation of yeast as shown in the production of carbon dioxide is accelerated by the presence of toluene and inhibited by chloroform or by a mixture of toluene and ethyl acetate. The initial rate of production of carbon dioxide by dried yeast is reduced by the addition of dextrose. The auto-fermentation of fresh yeast is

slightly inhibited at  $pH$  6.3 by lactose which has little effect on the fermentation of dextrose. It is also inhibited markedly by sodium chloride. Alcohol as well as carbon dioxide is produced during the fermentation. The yeast gum is not attacked, but the yeast glycozen shows a marked decrease in quantity during autofermentation.

W. O. K.

**Effect of Infinitesimal Traces of Chemical Substances on Photosynthesis.** J. C. BOSE (*Nature*, 1923, 112, 95-96).—The usual method of measuring the rate of photosynthesis of water-plants by counting the bubbles of oxygen evolved being untrustworthy, a device has been perfected whereby the evolution of equal volumes of oxygen is automatically recorded on a revolving drum. A definite relation has been found between the evolution of oxygen and the formation of carbohydrate in the leaf. In view of the fact that the coefficient of photosynthetic activity of the aquatic plant *Hydrilla verticillata* was doubled after a thunder-storm, presumably on account of the addition of traces of nitric acid, experiments were conducted which showed that the application of a solution of nitric acid at a dilution of 1 in  $10^{11}$  induced no change, 1 in  $10^{10}$  produced an increase in activity of 100%, whilst 1 in  $2 \times 10^9$  caused a further increase of nearly 200%. Similar increases in carbon assimilation were obtained by the application of dilute solutions of extract of thyroid gland, and formaldehyde. Of the latter substance, a solution containing 1 part in  $10^9$  parts caused an increase of photosynthetic activity of 85%. A. A. E.

**The Reaction of Protoplasm to some Reagents.** WILLIAM SEIFRIZ (*Ann. Bot.*, 1923, 37, 489-509).—Experiments on the effect of ethyl alcohol and the glucosides, saponin, smilacin, and senegin, respectively, on the protoplasm of the leaf-cells of *Elodea*. The initial effect of ethyl alcohol is an increase in permeability with exosmosis, resulting in lowering of osmotic pressure. This is followed by partial decrease in permeability and increase in osmotic pressure. The ultimate effect is coagulation and death of the protoplasm. The glucosides at first cause increased permeability and decrease of osmotic pressure. Longer treatment results in increase of osmotic pressure. Different theories of permeability and narcosis are discussed.

G. W. R.

**Influence of Ammonium Sulphate on Plant Growth in Nutrient Solutions and its Effect on Hydrogen-ion Concentration and the Availability of Iron.** LINUS H. JONES and JOHN W. SHIVE (*Ann. Bot.*, 1923, 37, 355-377).—A study of the effect of ammonium sulphate on the growth of soja beans in nutrient solutions and on the availability to plants of different forms of iron. In the solutions where nitrogen was supplied as nitrate, a decrease in hydrogen-ion concentration as a consequence of plant growth was observed. Where ammonium sulphate was substituted for nitrate an increase in hydrogen-ion concentration occurred. The availability of ferric phosphate was greater in the solutions containing ammonium sulphate than in those containing nitrates. Ferrous sulphate shows greater toxicity in the presence of ammonium

sulphate than in the presence of nitrate. Availability of iron compounds is apparently dependent on the changes in reaction of nutrient solutions induced by contact with plant roots. G. W. R.

**The Soluble Carbohydrates in Wheat Grains during Growth.**

H. COLIN and H. BELVAL (*Compt. rend.*, 1923, 177, 343—346).—Immature wheat grains contain 6% of levosin (cf. Tauret, A., 1891, i, 661), 1.5% of sucrose and less than 1% of a reducing sugar, these constituting all the (soluble) reserve carbohydrates (starch, 5—6%). As maturity is approached, starch is formed in increasing quantities (50—60%), the soluble carbohydrates lose their importance and their relative proportions change. The rotatory powers before and after inversion steadily increase, and the dextrose : laevulose ratio gradually approaches unity. At maturity, only 0.15% of free reducing sugar, 0.40% of crystallisable sugar and roughly the same amount of levosin are present. E. E. T.

**Phytochemical and Pharmacological Examination of the Seeds of *Chydenanthus excelsus*, Miers.** M. DUYSFAR (*Pharm. Weekblad*, 1923, 60, 777—799).—The tree is common in the Dutch Indies; the fruit and flowers are described in detail. The seeds contain a fatty oil, gallic acid, and a crystalline glucoside, *chydenanthin*,  $C_{21}H_{34}O_{10}$ . Hydrolysis separates this into arabinose, galactose, and a mixture of sapogenins, from which one, *chydenanthegenin*,  $C_{12}H_{20}O_3$ , was separated and recrystallised; it contains two hydroxyl groups and an aldehyde group.

The action of strong acids on chydenanthin gives an amorphous substance,  $C_9H_{15}O_4$ , containing three hydroxyl groups; nitric acid, however, yields picric acid, whilst potassium hydroxide yields valeric and oxalic acids.

Chydenanthin possesses strong hæmolyzing action, coagulates the blood in low concentrations, acts as a poison on the heart, and depresses the blood pressure. S. I. L.

**Comparative Plant Chemistry. VI. The Fruits of**

*Gleditschia triacanthos*, L. BINEM ASZKENAZY (*Monatsh.*, 1923, 44, 1—8).—*Seeds*. Extraction with light petroleum showed the presence of an oil, which on oxidation with permanganate gave dihydroxystearic acid (m. p. 129.5—130.5°), sativic acid (m. p. 172—174°), and an isomeric tetrahydroxystearic acid (?) (m. p. 158°). The oil therefore consisted of a mixture of acids of the oleic and linoleic type, no linolenic acids being present, and only very small quantities of solid acids. A *phytosterol*,  $C_{30}H_{50}O.0.5H_2O$ , was also isolated as leaflets, m. p. 152—153° (in closed tube). It is remarkable in possessing water of crystallisation (removable at 130°), in being optically inactive, and in being stable on exposure, in spite of the presence of two ethylenic linkings. The *acetyl* derivative forms leaflets, m. p. 164° (in closed tube).

Alcohol extracted only small quantities of material, which reduced Fehling's solution, was dextrorotatory, and gave no osazone. It is possibly allied to glycyrrhizin. The extract may have contained choline.

The hot aqueous extract was a viscous liquid, becoming a gel on cooling.

Proteins are present to a greater extent in the cotyledons than in the endosperm. The dried seeds contain: ether-soluble material, 4.08%; water-soluble material, 30.0%; water-soluble inorganic matter, 3.3%; raw fibre, 11.07%; pentosans, 7.95%; total ash, 3.78%; crude proteins, 22.81%. The weight unaccounted for (23%) is presumably due to polysaccharides which are insoluble in water.

*Husks.* These contain a phlobaphen and tannins, both of the protocathechuic type, dextrose, acetic acid, etc., the results of a complete analysis giving ether-soluble material, 1.67%; alcohol-soluble material, 26.00%; water-soluble material, 3.43%; soluble inorganic matter, 1.05%; raw fibre, 37.78%; pentosans, 12.41%; crude proteins, 7.81%; total ash, 4.11%. The 8% not accounted for is probably due to hemicelluloses of a non-pentosan type.

E. E. T.

**The Chemical Constituents of Green Plants. XXVIII.**  
**The Acids of the Tamarind (*Tamarindus indica*) Precipitable by Lead Acetate.** HARTWIG FRANZEN and HANS KAISER (*Z. physiol. Chem.*, 1923, **129**, 80—94).—The acids of the tamarind precipitable by lead acetate consist very largely of tartaric acid, small amounts of malic acid, and traces of oxalic acid, succinic acid, and citric acid.

W. O. K.

**Diurnal Variations in the Total Nitrogen Content of Foliage Leaves.** ALBERT CHARLES CHIBNALL (*Ann. Bot.*, 1923, **37**, 511—518).—From a review of published results it is concluded that a withdrawal of nitrogen from leaves takes place at night. G. W. R.

**The Constituents of Peach Leaves.** TATSUO KARIYONE and YUSHIRO KIMURA (*J. Pharm. Soc. Japan*, 1923, No. **494**, 247—251; cf. Bourquelot and Fichtenholz, A., 1910, ii, 742; 1911, i, 803; ii, 142).—Analysis of leaves of *Pyrus sinensis*, Lindl. (I), and *Pyrus communis*, L. (II), gave the following results: I. (collected in July and September, respectively): Water, 57.86%, 49.79%; Ash, 8.00%, 2.96%; Arbutin in dried leaves, 0.30%, 0.17%; Tannin (by Schröder's method), 2.41%, 2.91%. II. Corresponding figures (for July) are: 58.26%; 2.21%; 0.58%; 8.14%. K. K.

**The Chemical Constituents of Green Plants. XXIX.**  
**Some Water-soluble Constituents of the Leaves of the Bramble (*Rubus fruticosus*).** HARTWIG FRANZEN and ERNST KEYSSNER (*Z. physiol. Chem.*, 1923, **129**, 309—319).—By the use of the ester-hydrazide method, the following acids have been found in bramble leaves: lactic acid (0.8%), succinic acid (0.009%), malic acid (0.00015%), oxalic acid (0.0003%). The figures refer to the quantities present in the dry leaf and are only approximate. In addition, the copper salt of an unidentified acid, and two unidentified hydrazides of m. p. 181—182° and 201—202°, respectively, have also been isolated.

W. O. K.

**Presence of Quercitrin in the Leaves of *Camellia theifera* and in Dried Tea.** J. J. B. DEUSS (*Rec. trav. chim.*, 1923, 42, 623—624).—The presence of quercitrin in the fresh leaves of *Camellia theifera* and in dried tea may be demonstrated as follows. An aqueous extract of the material is filtered, treated with 1–2% of concentrated hydrochloric acid, and boiled under a reflux condenser while a rapid current of carbon dioxide is passed through. A brown precipitate is formed, and after about one to two hours the reaction is complete. The precipitate is washed with water and dried at 100° and extracted with ether, when the quercetin is removed and crystallised from water. Since the leaves contain no quercetin, this substance must have been formed by the hydrolysis of quercitrin in the leaves and consequently its formation constitutes a proof of the presence of the latter substance. The amount of quercitrin present is found to be about 0.1% and the amount is the same whether the leaves have been grown in the shade or exposed to the sunlight. J. F. S.

***Rapanea latavirens*, Mez.** E. HERRERO DUCLOUX and MAX AWSCHALOM (*Anal. Asoc. Quim. Argentina*, 1923, 11, 6—24).—The bark of *Rapanea latavirens*, Mez., contains 59.552% of moisture. The dry matter contains ash 10.355%, total nitrogen 1.335%, proteins, 8.347%, crude fat 3.093%, cellulose 21.352%, carbohydrates 56.853%. The isolation of the acid and neutral saponin, respectively, is described and their reactions with a number of reagents are given. The neutral saponin was found to be more toxic to fish and to have a greater hæmolytic power than the acid saponin. The dry matter contains acid saponin 0.809% and neutral saponin 0.213%. G. W. R.

**Chemistry of Japanese Plants. I. The Proximate Composition of Karafuto Wood.** HISASHI NAKAMURA (*Mem. Coll. Sci. Kyoto*, 1923, 6, 295—304).—Sawdust from the wood of two species of tree growing in the forests of the island of Karafuto was examined by hydrolysis for sugars, pentosans, and hexosans, lignin, and cellulose. Very little difference was found in the proximate analyses of the two woods. *d*-Mannose, *d*-galactose, and *l*-xylose were found in the acid extract after hydrolysis; the first being actually isolated in the crystalline state. H. H.

**The Presence of Urease in the Nodules on the Roots of Leguminous Plants.** E. A. WERNER (*Nature*, 1923, 112, 202).—The presence of urease has been demonstrated in the nodules from the rootlets of *Trifolium procumbens*, *T. pratense*, *T. repens*, *Vicia sativa*, *Medicago sativa*, *Galega officinalis*, various lupins, and the garden pea. Urease was not found in any roots devoid of nodules, but it was clearly present in the cylindrical tuberosous growths developed from the rootstock of *Ranunculus ficaria*. A. A. E.

**The Presence of Loroglossine in Eleven New Species of Indigenous Orchids.** P. DELAUNAY (*Bull. Soc. Chim. biol.*, 1923, 5, 398—408; cf. A., 1921, i, 801).—Loroglossine has been isolated from a further eleven species of orchids. E. S.

**Extraction and Separation of the Pigments of *Nereocystis luetkeana*.** GRACE E. HOWARD (*Publ. Puget Sound Biol. Sta.*, 1921, 3, 79—91).—Chlorophyll-A and -B, carotene, xanthophyll, and fucoxanthin can be extracted by Willstätter's method, but not with pure solvents. Colloidal chlorophyll carries a negative charge. Magnesium is present in chlorophyll, and chlorophyllase is probably present in kelp. CHEMICAL ABSTRACTS.

**Soil Structure and Colloid Chemistry.** G. HAGER (*Z. Pflanz. Düng.*, 1923, 2, 292—311).—Theoretical. A discussion of the bearing of the phenomena of adsorption on soil structure with particular reference to the work of Mattson (A., 1922, i, 800). G. W. R.

**Arable Soil: Natural Zeolites.** F. SCURTI (*Ann. Chim. Appl.*, 1923, 13, 161—193).—The published analytical results of natural zeolites show that, in their typical forms at least, these compounds are alkali or alkaline earth salts of dimeta-*n*-ortho-silico-aluminic acids. The number of silicon atoms present is sometimes ten, but as yet no zeolites with eight atoms of silicon are known. As regards the water present, zeolites containing up to six atoms of silicon tend to absorb water extraneous to the mineral itself. As the silicon atom chain lengthens further, this process undergoes inversion, zeolites with seven atoms of silicon containing less than the theoretical proportion of water. The tendency to absorb water is evidently due to the aluminic hydroxyl groups and that to lose water to the silicic hydroxyl groups. The presence of these hydroxyls of different types explains the ability of zeolites to unite with either acids or bases and also the ease with which the alkali or alkaline-earth metal is replaceable by other metals or by ammonia. In this exchange, no matter what the concentration of the salt used, the new ion never replaces the original metal completely, the tendency of the new products to act in the inverse sense resulting in the establishment of a condition of equilibrium.

In such processes may be sought the general mechanism of the fixation of bases in arable soil, the absorbent power of the soil being interpreted as a true chemical combination obedient to the laws of mass action rather than as a physical absorption comparable with that of water by a sponge. The reactions of the zeolites also furnish ready explanations of the formation of alkaline soils and of the increase of acidity sometimes effected in soils. T. H. P.

**Comparison of Active Aluminium and Hydrogen-ion Concentration of Widely Separated Acid Soils.** PAUL S. BURGESS (*Soil Sci.*, 1923, 15, 407—412).—From an examination of a large number of acid soils from different localities in the United States, it is concluded that there is a general correlation, with individual exceptions, between the content of active aluminium and hydrogen-ion concentration. [See, further, *J.S.C.I.*, 1923, 846A.]

G. W. R.

**Variability of Nitrates and Total Nitrogen in Soils.** ARTHUR L. PRINCE (*Soil Sci.*, 1923, 15, 395—405).—A study of the variability of certain soils in total and nitrate nitrogen. It

is shown that the variability in nitrate content and nitrifying power is much greater than the variability in total nitrogen and a correspondingly larger number of samples must be taken in the former case in order to obtain trustworthy results. [See, further, *J.S.C.I.*, 1923, 846A.]  
G. W. R.

**The Relation of Concentration of Soil Solution to Nitric Nitrogen in Soils containing Large Quantities of Available Nitrogen and their Effect on Plant Growth.** (*New Mexico Agr. Exp. Sta. Ann. Rep.*, 1921, 24—25).—Soil which contains an excessive quantity of nitrates contains also other soluble salts in excessive quantities. As the quantity of total salts increased, the nitrate increased more rapidly. Injury is due chiefly to sulphates and chlorides rather than to nitrates. CHEMICAL ABSTRACTS.

**Some Relations of Organic Matter in Soils.** F. A. CARLSON (*Cornell Agr. Exp. Sta. Mem.*, 1923, 61).—Experiments with Dunkirk clay loam showed that plots in rotation with legumes contained more nitrogen than plots in rotation without legumes, the increase being greater in limed plots than in unlimed. There is a close relation between organic carbon and nitrogen.

CHEMICAL ABSTRACTS.

**[Incorporation of] Organic Matter [in Soils].** F. J. SIEVERS (*Washington Agr. Expt. Sta. Bull.*, 1922, 167, 45—46).—The incorporation of straw having a nitrogen : carbon ratio of 1 to 75 in the soil produced a depressing effect on nitrate development, which persists until there is sufficient decomposition to cause the ratio to approach that in the soil, 1 to 13. When organic matter having a narrow nitrogen : carbon ratio like legumes is incorporated in the soil there is a rapid development of nitrate. There is less loss of carbon dioxide and indication of greater organic matter maintenance.

CHEMICAL ABSTRACTS.

**The Influence of Precipitation on Soil Composition and on Soil Organic Matter Maintenance.** F. J. SIEVERS and H. F. HALTZ (*Washington Agr. Expt. Sta. Bull.*, 1923, 176).—Soils receiving about 20.3 cm. of precipitation annually contain about one-fourth as much nitrogen in the surface layer 15.24 cm. deep as those receiving about 50.8 cm. annually. The ratio between the nitrogen and carbon remains practically constant. Variations in precipitation have no influence on the amount of total phosphorus and potassium in the soil, but that of the calcium (present as silicate) is slightly influenced; the organic matter content of the subsoil shows little change. The nitrogen : carbon ratio for the subsoil is slightly narrower than that for the corresponding surface soil.

CHEMICAL ABSTRACTS.

## Organic Chemistry.

**New Zealand Mineral Oils.** THOMAS H. EASTERFIELD and NORMAN McCLELLAND (*Chemistry and Industry*, 1923, **42**, 936—938).—Three classes of mineral oil have been manufactured in New Zealand. Kauri oil is obtained by the distillation of peat containing kauri gum and is a mixture as complex as crude rosin oil. There are large deposits of oil shale in the Southland District and natural mineral oil occurs in many localities. The only considerable flow occurs at New Plymouth. This oil contains an unusually high percentage of solid paraffins, 12–13%, and the various fractions have generally higher specific gravities than fractions of similar boiling point from other sources. In the “benzine” fraction the following cycloparaffins have been identified: methylcyclopentane, cyclohexane, methylcyclohexane,  $\alpha$ -decanaphthene, undecanaphthene, and dodecanaphthene. The aromatic hydrocarbons identified were benzene, toluene, the three xylenes, naphthalene,  $\alpha$ -methylnaphthalene, and 1:4-dimethylnaphthalene. The oil is practically free from sulphur and acid and basic constituents. The paraffins from  $C_{24}H_{50}$  to  $C_{31}H_{64}$ , excluding  $C_{27}H_{56}$ , were all identified. The paraffins are not decomposed by heating for a week in a vacuum at 350–400°. E. H. R.

**The Addition of Water to Ethylene and Propylene.** J. P. WIBAUT and J. J. DIEKMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 321–328).—The reversibility of the dehydration of ethyl and *n*-propyl alcohols by means of alumina or aluminium sulphate at 300–400° has been studied, and very small quantities of acetaldehyde and acetone, respectively, were detected in the reaction mixture of olefine and water vapour after it had been passed over the heated catalyst. It is thought that water unites with ethylene to give ethyl alcohol which immediately decomposes into acetaldehyde and hydrogen. Similarly, in conformity with Markovnikov's rule, water unites with propylene to give isopropyl alcohol, which immediately breaks down into acetone and hydrogen.

Experiments were also carried out on the absorption of ethylene and propylene by means of sulphuric acid at various temperatures and concentrations, but only very small yields of ethyl and isopropyl alcohols were obtained.

H. H.

***n*-Amylethylene [ $\Delta^8$ -Heptene] Oxide from Heptaldehyde.** JULIUS VON BRAUN and WERNER SCHIRMACHER (*Ber.*, 1923, **56**, [B], 1845–1850).—The fission of cholines (cf. Meyer and Hopff, A., 1921, i, 851; Karrer and Horlacher, A., 1922, i, 825) has been investigated in the hope that, in suitable cases, it might lead to  $\alpha\beta$ -unsaturated alcohols. This does not appear to happen with the quaternary bases derived from  $\beta$ -dimethylaminoheptyl alcohol, which unexpectedly yields almost exclusively  $\Delta^8$ -heptene oxide.

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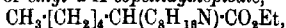
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The production of an unsaturated alcohol is not observed when the dimethylamino-group is replaced by the *A*- or *B*-copellidyl residue.

Heptaldehyde is converted successively into heptonic acid and ethyl  $\alpha$ -bromoheptanoate. The latter compound, when treated with dimethylamine dissolved in benzene, yields *ethyl  $\alpha$ -dimethylaminoheptanoate*, an almost colourless liquid, b. p. 100°/10 mm. (*methiodide*, m. p. 126°). The ester is reduced by sodium and alcohol to  $\beta$ -*dimethylaminoheptyl alcohol*,  $\text{CH}_3\text{Me} \cdot [\text{CH}_2]_4 \cdot \text{OH}(\text{NMe}_2) \cdot \text{CH}_2 \cdot \text{OH}$ , a colourless liquid, b. p. 97–98°/10 mm. (the non-crystalline *hydrochloride*, the *picrate*, m. p. 98°, and the *methiodide*, m. p. 122°, are described). The methiodide is transformed by silver oxide into the corresponding hydroxide which when heated under diminished pressure yields  $\Delta^2$ -heptene oxide,  $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$ , b. p.

143–145°,  $d_4^{25}$  0.8385,  $n_D^{25}$  1.4164. It is converted by dilute sulphuric acid into heptaldehyde and by water at 180° into *heptene  $\alpha$ -glycol*,  $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , a colourless, viscous liquid, b. p. 128–130°/11 mm. Fuming hydrochloric acid transforms the oxide into  $\alpha$ -chloro- $\beta$ -hydroxy-*n*-heptane, a colourless liquid, b. p. 87–88°/10 mm.;  $\alpha$ -bromo- $\beta$ -hydroxy-*n*-heptane, b. p. 102–103°/12 mm., is prepared in a similar manner.  $\Delta^2$ -Heptene oxide and dimethylamine in the presence of benzene yield  $\alpha$ -dimethylamino- $\beta$ -hydroxy-*n*-heptane, b. p. 83–85°/11 mm. (*picrate*, m. p. 63–65°; *methiodide*, m. p. 106–108°); the compound is also obtained from  $\alpha$ -chloro- or  $\alpha$ -bromo- $\beta$ -hydroxy-*n*-heptane by the action of dimethylamine.

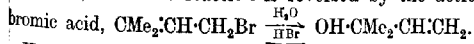
The action of *A*-copellidine on ethyl  $\alpha$ -bromoheptanoate leads in part to the loss of hydrogen bromide from the latter and in part to the formation of *ethyl  $\alpha$ -A-copellidylheptanoate*,



a moderately mobile liquid, b. p. 160–163°/10 mm.,  $d_4^{20}$  0.9274, which yields only non-crystalline derivatives. *Ethyl  $\alpha$ -B-copellidylheptanoate* has b. p. 160–163°/10 mm.,  $d_4^{20}$  0.9326; its derivatives could not be caused to crystallise. Reduction of the esters by sodium and ethyl alcohol leads smoothly to the production of  $\alpha$ -*A-copellidylheptyl alcohol*, a viscous liquid, b. p. 163–166°/11 mm. (which gives only non-crystalline derivatives) and  $\alpha$ -*B-copellidylheptyl alcohol*, b. p. 163–166°/11 mm., which does not yield well-defined derivatives. The bases are converted into their methiodides and thence into the corresponding quaternary hydroxides, which are distilled under diminished pressure. The basic products of the reaction consist of mixtures of *A*- and *B-copellidylheptyl alcohols* with *A*- and *B-N-methylcopellidines*, respectively (the substances will be described in detail in a subsequent communication); the non-basic product is  $\Delta^2$ -heptene oxide, the amount of which corresponds with that of the 1-methylcopellidine simultaneously formed. H. W.

**Abnormal Reactions of Derivatives of Isoprene and of  $\beta$ -Dimethylbutadiene.** L. CLAISEN, F. KREMERS, F. ROTH, and E. TIETZE (*J. pr. Chem.*, 1922, [ii], 105, 65–92, 288).—The action of gaseous hydrogen bromide on ice-cold isoprene leads

primarily to the formation of the tertiary bromide,  $\text{CMe}_2\text{Br}\cdot\text{CH}\cdot\text{CH}_2$ . The product has b. p. indefinite, largely below  $50^\circ/40$  mm., if an excess of hydrogen bromide is avoided and the distillation is carried out soon after the bromination; but if the product is kept a few hours before distillation, and particularly if hydrogen bromide is present, it is converted into the primary bromide,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ , b. p.  $50\text{--}51^\circ/40$  mm., or  $62\text{--}64^\circ/67$  mm. The constitution of the latter, which Mokiewsky (A., 1900, i, 509) regarded as the tertiary bromide, is proved as follows. It reacts in warm benzene solution with the sodio-derivative of formanilide, giving *formo-N- $\Delta^2$ -isopentenylanilide*, a thick oil, b. p.  $163\text{--}164^\circ/16\cdot5$  mm.,  $d_{20}^{25} 1\cdot029$ , which is hydrolysed by boiling with concentrated methylalcoholic potassium hydroxide to *N- $\Delta^2$ -isopentenylaniline*, an oil, b. p.  $136\text{--}137^\circ/16\cdot5$  mm.,  $d_{20}^{25} 0\cdot9583$ . The latter is benzoyleated by warming with pyridine and benzoyl chloride, giving *benzo-N- $\Delta^2$ -isopentenylanilide*, hard, colourless rods, m. p.  $80\text{--}81^\circ$ , which is reduced by the aid of hydrogen and palladium to *benzo-N-isoamylanilide*, long, hard rods, m. p.  $75^\circ$ , identical with the product formed by benzoyleating *isoamylaniline*. The primary bromide reacts with magnesium phenyl bromide to give  $\Delta^2$ -isopentenylbenzene ( $\gamma$ -dimethylallylbenzene) (Klages, A., 1906, i, 661), which is also prepared by the action of magnesium methyl iodide on ethyl hydrocinnamate, the dehydration of the intermediately formed carbinol being accomplished by distilling it with ammonium iodide, and then with phosphoric oxide. *isoPentenylbenzene* reduces mercuric acetate, although, according to Balbiano (A., 1915, i, 426), this is characteristic of aromatic propenyl derivatives, but not of allyl or  $\Delta$ -butenyl derivatives. *isoPentenylbenzene* is converted into  $\gamma$ -dimethylpropenylbenzene, when boiled with a small quantity of alkali hydroxide; when heated at  $100^\circ$  with hydrogen bromide in glacial acetic acid solution, it gives a colourless *hydrobromide*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Br}$ , b. p.  $126\text{--}128^\circ/14$  mm. The primary bromide is converted by the action of alcoholic sodium ethoxide solution into ethyl  $\Delta^2$ -isopentenyl ether, a colourless liquid, b. p.  $124\cdot7\text{--}125^\circ$ ,  $d_{20}^{25} 0\cdot8005$ , which is apparently identical with the ether previously described by Ipatiev (A., 1899, i, 657), and is reduced by means of palladium-hydrogen in alcoholic solution to ethyl *isoamyl* ether. The primary isoprene hydrobromide is unusually unstable towards water, being almost completely decomposed within thirty minutes with formation of the tertiary alcohol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2$ . The latter (Mokiewsky, *loc. cit.*) is evidently produced directly, and not by isomerisation of the primary alcohol,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ , since this (Courtot, A., 1906, i, 788) shows no tendency to pass into its isomeride. The production of the alcohol from the bromide is best carried out in the presence of sodium carbonate, since the reaction is reversed by the action of hydro-



Hydrogen bromide reacts with cold  $\beta$ -dimethylbutadiene to give  $\alpha$ -bromo- $\beta$ -dimethyl- $\Delta^2$ -butylene,  $\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ , a colourless, lachrymatory liquid, b. p.  $51\text{--}54^\circ/20$  mm.,  $62\text{--}65^\circ/31$  mm.,

or 144—148° (decomp.) at the ordinary pressure, which is readily decomposed by the action of water, and reacts with bromine in chloroform solution to give an oily (†) *dibromide*, which gradually loses hydrogen bromide at the ordinary temperature, and passes on distillation into an oily compound,  $C_6H_{10}Br_2$ , b. p. 115—119°/14 mm. (cf. Courtot, *loc. cit.*). In the formation of the primary bromide, the tertiary bromide,  $CMc_2Br \cdot CMe:CH_2$ , is evidently first produced, since the product has a low b. p., 27—50°/20 mm., if it is distilled soon after being prepared. The prolonged action of hydrogen bromide on ice-cold dimethylbutadiene gives a *dihydrobromide*, probably  $CMc_2Br \cdot CHMe \cdot CH_2Br$ , crystals resembling ammonium chloride, which volatilises at 160—180°. The primary bromide is converted by the action of sodium carbonate solution into the tertiary alcohol,  $\alpha\beta$ -trimethylallyl alcohol (Courtot, *loc. cit.*), which gives a *benzoate*, a thick oil, b. p. 126—127°/12 mm.; the latter quickly decomposes into benzoic acid and dimethylbutadiene when heated under the ordinary pressure. The primary bromide reacts with sodium ethoxide to give the *ethyl ether*, b. p. 143—143.2°/757 mm.,  $d_{15}^{20}$  0.8167, and with magnesium phenyl bromide to give  $\beta$ -*dimethyl- $\Delta^2$ -butenylbenzene*,  $CH_2Ph \cdot CMe:CMc_2$ , b. p. 220—221°/750 mm.,  $d_{15}^{20}$  0.903. The latter is converted by the action of hydrogen bromide in glacial acetic acid solution at 100° into a *hydrobromide*,  $C_6H_{12}PhBr$ , b. p. 134—136°/15 mm., and is reduced by means of palladium-hydrogen to  $\beta$ -*dimethylbutylbenzene*, b. p. 216.5—217.5°/755 mm.,  $d_{15}^{20}$  0.8765. *Formo- $\beta$ -dimethyl- $\Delta^2$ -butenylanilide*, a viscous oil, b. p. 169—171°/16 mm., is produced like the *isopentenyl* derivative, and is hydrolysed by means of methyl-alcoholic potash to  $\beta$ -*dimethyl- $\Delta^2$ -butenylaniline*, b. p. 144—146°/16.5 mm.,  $d_{15}^{20}$  0.9622, which readily gives a *benzoyl* derivative, hard, quadratic tablets, m. p. 97.5—98.5°. The action of an ethereal solution of aniline on a light petroleum solution of  $\beta$ -*dimethyl- $\Delta^2$ -butenyl bromide* gives aniline hydrobromide and a substance, rods grouped in rosettes, m. p. 58—59°, perhaps *di- $\beta$ -dimethyl- $\Delta^2$ -butenylaniline*.  
W. S. N.

**The Preparation of Acetylenic Hydrocarbons by the Electrolysis of Unsaturated Acids.** MARCEL BOUIS (*Bull. Soc. chim.*, 1923, [iv], 33, 1081—1084).—Electrolysis of a 40% aqueous solution of sodium acrylate by means of a current of 3 amperes leads to the formation of acetylene, which is identified by means of its reactions and the formation of its tetrabromide. The composition of the electrolytic gas in several experiments was determined and found to be:  $CO_2$ , 68—76%;  $C_2H_2$ , 4—8%;  $O_2$ , 7—16%;  $CO$ , 8—13%. Similarly, sodium crotonate gives allylene, identified by means of its silver compound. The composition of the electrolytic gas is much the same in both cases.  
H. H.

**The Components of Wood Spirit Oil.** H. PRINGSHEIM and J. LEIBOWITZ (*Ber.*, 1923, 56, [B], 2034—2041).—The separation of wood spirit oil (the residue left after the isolation of methyl alcohol from wood spirit) cannot be effected advantageously by fractional distillation under atmospheric pressure, since the oxidisable

nature of the substances prevents the use of a long column, whilst under diminished pressure the separation is very incomplete. By combining the two methods, it is, however, possible to isolate methyl ethyl ketone, methyl propyl ketone, and dipropionylethane.

More promising results are obtained by treating the oil with sodium hydrogen sulphite solution, whereby it is separated into crystalline additive compounds (aldehydes and methyl ketones), compounds which are soluble in the solution (mesityl oxide and similar unsaturated ketones), and undissolved oil (hydrocarbons, alcohols, etc.). The crystalline compounds have been examined by decomposing the precipitate with dilute sulphuric acid, separating the liberated aldehydes and ketones as far as possible by fractional distillation, and converting them into crystalline derivatives. The presence of the following substances is established: *xx*-dimethylpropaldehyde,  $\text{CMe}_3\text{CHO}$ , b. p.  $74^\circ$ ; methyl ethyl ketone; isovaleraldehyde; methyl isopropyl ketone;  $\Delta^7$ -hexene- $\beta$ -one,  $\text{CH}_3\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\text{Me}$ ; cyclopentanone.

$\Delta^7$ -Hexene- $\beta$ -one, b. p.  $122$ – $124^\circ$ , is isolated with some difficulty, since it decomposes readily at a moderate temperature; with *p*-nitrophenylhydrazine it gives a crystalline derivative,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_3$ , m. p.  $126^\circ$ . Its constitution is deduced from the observation that it is oxidised by potassium permanganate in the presence of acetone to pyruvic and propionic acids.

Treatment of the oil with potassium hydroxide solution which is subsequently acidified leads to the isolation of a single acid,  $\text{C}_8\text{H}_{16}\text{O}_4$ , a colourless liquid, b. p.  $46^\circ/0.8$  mm. Analysis of the corresponding silver salt and of the derivative,  $\text{C}_{22}\text{H}_{31}\text{O}_7\text{N}_3$ , colourless needles, m. p.  $198^\circ$ , shows it to be a dihydroxyoctanemonocarboxylic acid. It is reduced by hydriodic acid and phosphorus to an octoic acid,  $\text{C}_8\text{H}_{16}\text{O}_2$ , b. p.  $200$ – $210^\circ$  (decomp.). H. W.

**The Photo-oxidation of Alcohol. III. The Catalytic Influence of some Ketones on the Photo-oxidation of Ethyl Alcohol.** W. D. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 443–455; cf. A., 1921, ii, 500).—The action of thirty-four ketones in promoting the photo-oxidation of ethyl alcohol was studied, and some general conclusions were drawn from the results. The velocities of activation appear to be independent of the concentration of ketone within fairly wide limits. The photo-activity of monoketones appears to be definitely associated with their aromatic character.  $\alpha\beta$ -Diketones are especially active, whereas  $\alpha\beta\gamma$ -triketones are inactive. The inactivity of the last class is ascribed to the possibility of the central carbonyl group forming an oxonium salt with the alcohol, thereby destroying the photocatalytically active double  $\alpha\beta$ -diketonic structure. H. H.

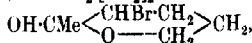
**The Unsaturated Reduction Products of Sugars and their Transformations. VI.  $\delta$ -Hydroxyacetylbutyl Alcohol, a Simple Ketose.** MAX BERGMANN and ARTHUR MIEKELEY (*Annalen*, 1923, 432, 319–344; cf. A., 1921, i, 763; 1922, i, 618; this vol., i, 653).—It has previously been observed (A., 1922, i, 618) that the cycloacetal of  $\delta$ -acetyl-*n*-butyl alcohol is remarkably sensitive

towards dilute mineral acids, a fact which illustrates the impossibility of distinguishing between the  $\alpha\beta$ - and  $\alpha\delta$ -oxide structures by means of their stability. A striking contrast is presented by the behaviour of the dicyclic anhydride of  $\delta$ -hydroxy- $\delta$ -acetyl-*n*-butyl alcohol, which, although it contains an ethylene oxide ring, is unusually resistant to fission by means of hydroxylic reagents.

The oxidation of anhydroacetylbutyl alcohol in dry ethereal solution by means of perbenzoic acid gives  $\beta\gamma$ - $\beta\zeta$ -dioxidohexane,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} > \text{O}$ , a colourless liquid, b. p.  $56.5-57.5^\circ/12$  mm.,  $d_4^{20}$  1.0331,  $d_4^{25}$  1.0326,  $n_D^{20}$  1.4441,  $n_D^{25}$  1.4438, *phenylhydrazone*, m. p.  $85-86^\circ$ . This dicyclic anhydride reduces hot Fehling's solution, but does not give a red coloration with a pine shaving. It is stable towards methyl alcohol, or even towards water at  $130^\circ$ . If the oxidation is conducted in moist ethereal solution, the product is  $\delta$ -hydroxy- $\delta$ -acetylbutyl alcohol,  $\text{OH}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CMe}$ , or  $\text{OH}\cdot\text{CMe}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CMe}$ , m. p.  $73^\circ$  (sinters at  $70^\circ$ ), b. p.

$143-144^\circ/11$  mm., which reduces Fehling's solution even in the cold, and forms a *phenylosazone*, slightly yellowish-brown needles, m. p.  $133^\circ$ . It is converted into its anhydride by distilling with benzoic acid under 15 mm. pressure; the reverse change is difficult to accomplish, but may be effected by boiling the anhydride with *N*-sulphuric acid. The action of 0.01*N*-methyl-alcoholic hydrogen chloride on hydroxyacetylbutyl alcohol gives  $\gamma$ -hydroxy- $\beta$ -methoxy-

$\beta\zeta$ -oxidohexane,  $\text{OMe}\cdot\text{CMe}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CMe}$ , a colourless liquid, b. p.  $76-77^\circ/9-10$  mm.,  $d_4^{20}$  1.0813,  $n_D^{20}$  1.4542,  $n_D^{25}$  1.4540, which has a slight odour resembling that of camphor or turpentine. This compound is also produced in poor yield by the action of 0.1*N*-methyl-alcoholic hydrogen chloride on dioxidohexane, together with  $\beta\gamma$ -dimethoxy- $\beta\zeta$ -oxidohexane, a colourless liquid, b. p.  $69-70^\circ/12$  mm.,  $d_4^{20}$  1.0300,  $n_D^{20}$  1.4400,  $n_D^{25}$  1.4397,  $n_D^{30}$  1.4405, which has a faint, camphoraceous odour and a bitter taste, and does not reduce Fehling's solution. The dimethoxy-derivative is converted by the action of 0.1*N*-hydrochloric acid at  $50^\circ$  into  $\delta$ -acetyl- $\delta$ -methoxybutyl alcohol, a syrup, b. p.  $88-90^\circ/1.5$  mm. The oxidation of the dimethoxy-compound by means of chromic acid gives  $\gamma$ -acetyl- $\gamma$ -methoxybutyric acid, a syrup, b. p.  $115^\circ/5$  mm. Acetobutyl alcohol forms a white *oxonium* salt with ferrocyanic acid, the addition of which to a mixture of acetobutyl alcohol and methyl alcohol rapidly effects the formation of the *cycloacetal*. A similar *oxonium* salt is obtained from dioxidohexane and ferrocyanic acid; its constituents are regenerated by the aid of alkali hydrogen carbonate solution and ether, but the action of a further quantity of dioxido-compound in methyl-alcoholic solution gives oxido- $\beta\gamma$ -dimethoxyhexane. The action of bromine (1 mol.) on an ice-cold chloroform solution of acetobutyl alcohol gives  $\delta$ -bromo- $\delta$ -acetylbutyl alcohol,  $\text{OH}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CHBrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{CMe}$ , or



a slightly yellow, lachrymatory liquid, b. p. 70—75°/1.5 mm., which reduces warm Fehling's solution. It readily loses hydrogen bromide, even when warmed with water, with production of a second *anhydride* of hydroxyacetylbutyl alcohol, a colourless liquid, b. p. 63—64°/24 mm., or 50—51°/12 mm.,  $n_D^{20}$  1.4381, which becomes discoloured in contact with air, and reduces Fehling's solution. It reacts with phenylhydrazine, giving an oil. Bromoacetylbutyl alcohol reacts immediately with aqueous phenylhydrazine acetate solution, to give the osazone of hydroxyacetylbutyl alcohol, and with warm, anhydrous methyl alcohol, with formation of  $\gamma$ -bromo- $\beta$ -methoxy- $\beta$ - $\gamma$ -oxidohexane,  $\text{OMe} \cdot \text{CMe} < \begin{smallmatrix} \text{CHBr} \cdot \text{CH}_2 \\ \text{O} \end{smallmatrix} > \text{CH}_2$ , an oil, b. p. 78—81°/14 mm. The second anhydride mentioned above reacts with boiling 0.1*N*-methyl-alcoholic hydrogen chloride, with formation of a liquid, b. p. 63—65°/12 mm. W. S. N.

**Alkylglycerols. II. Reactions of Alkylglycerols. Some Esters and Derivatives. III. Action of Organomagnesium Compounds on the Epibromohydrin of Ethylglycerol.** R. DELABY (*Ann. Chim.*, 1923, [ix], 20, 33—81; cf. this vol., i, 741).—A republication, with additions, of work previously described (cf. this vol., i, 289, 531, 646; ii, 264). The action of diethylamine on  $\alpha$ -dibromopentan- $\beta$ -ol yields a *tetraethyldiaminopentanol*, b. p. 136—138°/20 mm., *picrate*, m. p. 102—103°. Oxidation of  $\alpha\beta$ -dibromopentan- $\gamma$ -ol by sodium dichromate in dilute sulphuric acid results in formation of  $\alpha\beta$ -dibromopentan- $\gamma$ -one together with acetic and propionic acids, whilst  $\alpha\gamma$ -dibromopentan- $\beta$ -ol yields the corresponding pentanone and acetic acid. The following are described:  $\alpha\beta$ -dibromodecan- $\gamma$ -ol, b. p. 170°/12 mm., a *diethylaminophenylpentanol*, b. p. 150—155°/19 mm. H. J. E.

**The [Crystal] Structure of Pentaerythritol, and a Graphical Interpretation of Laue (Schichtlinien) Diagrams.** H. MARK and K. WEISSENBERG (*Z. Physik*, 1923, 17, 301—315).—The mathematical analysis is detailed of a geometrical method applicable to the determination of crystallographic structure from a Laue diagram photographed on a cylindrical surface. It is shown that pentaerythritol crystallises in the di-tetragonal pyramidal system, with respective axes of lengths  $a=6.16$  Å.,  $c=8.76$  Å. Moreover, the crystals belong to the space group type  $C_{4v}$ , and the elementary crystal cell is space-centred and contains two molecules,  $\text{C}_5\text{H}_{12}\text{O}_4$ . The symmetry of the molecule and of the central carbon atom is represented by  $C_{4v}$ . The four substitution groups  $\cdot\text{CH}_2\text{OH}$  are structurally equivalent and lie in the hemimorphic plane of symmetry. J. S. G. T.

**Hydrolysis of  $\beta\beta'$ -Dichlorodiethyl Sulphide and Action of Hydrogen Halides on Divinyl Sulphide.** SIDNEY HARTLEY BALES and STANLEY ARTHUR NICKELSON (*T.*, 1923, 123, 2486—2489).

**The Action of Methyl Iodide on Disulphides.** WILHELM STEINKOPF and SIEGFRIED MÜLLER (*Ber.*, 1923, 56, [2], 1926—1930).—The action of methyl iodide on dimethyl disulphide takes

place in accordance with the schemes:  $\text{MeS} \cdot \text{SMe} + \text{MeI} \rightarrow \text{SMe}_2 \cdot \text{SMeI} \rightarrow \text{SMe}_2 + \text{SMel}$ ;  $\text{SMe}_2 + \text{MeI} \rightarrow \text{SMe}_3\text{I}$ ;  $\text{SMel} + \text{MeI} \rightarrow \text{SMe}_2\text{I}_2 \xrightarrow{+\text{MeI}} \text{SMe}_3\text{I}_2$ . There does not appear to be any evidence of the formation of the radicle  $\text{SMe}$ . This conclusion is confirmed by the observation that diphenyl disulphide is attacked with greater difficulty by methyl iodide than is dimethyl disulphide, whereas dissociation into radicles, if possible, would be expected to occur more readily in the case of the diphenyl compound.

Dimethyl disulphide is transformed by more than four molar proportions of methyl iodide at  $100^\circ$  into trimethylsulphonium iodide, decomp.  $203-207^\circ$ , according to the manner of heating, and trimethylsulphonium tri-iodide, m. p.  $39^\circ$ . Dimethyl sulphide di-iodide (which can be obtained in the crystalline form, m. p.  $58-64^\circ$ , according to the mode of heating, by the gradual addition of concentrated aqueous hydriodic acid solution to dimethylsulphide) and methyl iodide at  $100^\circ$  yield trimethylsulphonium tri-iodide. Dimethyl disulphide is converted by methyl bromide at  $100^\circ$  into trimethylsulphonium bromide, decomp.  $172^\circ$ .

Diphenyl disulphide is converted by prolonged heating with methyl iodide at  $100^\circ$  into phenyldimethylsulphonium tri-iodide, m. p.  $53.5^\circ$ , and phenyl methyl sulphide; under the experimental conditions adopted, the latter substance does not unite with methyl iodide to give a sulphonium iodide.

H. W.

**Trimethylene Trisulphide.** O. HINSBERG (*Ber.*, 1923, 56, [B], 1850-1852).—In reply to Fromm and Schultis (this vol., i, 580), the author reaffirms that  $\beta$ -trithioformaldehyde, m. p.  $247^\circ$ , is a well-defined chemical individual which is transformed when warmed with solvents into the stable  $\alpha$ -variety, m. p.  $216^\circ$ . A second labile form of trithioformaldehyde also appears to exist; it has m. p.  $216^\circ$ , and passes when treated with solvents into the stable form of the same melting point. The theory of the sulphur atom is in harmony with these observations, since it predicts the possibility of the existence of four stereoisomeric trithioformaldehydes.

H. W.

**Ethyl Formate from Oxalic Acid, Glycerol, and Alcohol.** WILFRID B. S. BISHOP (*J. Soc. Chem. Ind.*, 1923, 42, 401-402r).—Ethyl formate is conveniently prepared by distilling 46 g. of ethyl alcohol into a mixture of 200 g. of glycerol, 90 g. of anhydrous oxalic acid, and 90 g. of the hydrated acid heated at  $105-110^\circ$ . The vapours formed are passed through a reflux condenser kept at  $62^\circ$  and a still-head at  $54-60^\circ$  into a condenser and receiver. The liquid collecting in the receiver is ethyl formate of commercial purity, and the yield is 80% of theory. When the temperature of the distilling liquid rises above  $68^\circ$ , the distillate is practically pure alcohol. The glycerol may be used for at least three fresh charges of oxalic acid and ethyl alcohol.

F. H. R.

**Fine Structure of some Sodium Salts of the Fatty Acids in Soap Curds.** S. H. PIPER and E. N. GRINDLEY (*Proc. Physical Soc.*, 1923, 35, 269-272).—The structure of the soap curds of

sodium laurate, sodium myristate, and sodium palmitate has been investigated by the X-ray method. The X-ray photographs show lines due to reflections from planes with very wide spacings of the order 40 Å. These planar spacings increase uniformly with the number of methylene groups in the molecule, the actual spacings observed in the three cases being 33.5, 38.5, and 43.5 Å., respectively, the addition of two methylene groups to the carbon chain giving an increase of 5 Å. This indicates that the effective length of the methylene group is 1.25 Å. These and other lines observed are to be accounted for by the assumption that the curds are in the smectic state described by Friedel (this vol., ii, 223).

J. F. S.

**The Microscopic Structure of Soap.** KENNETH MACLENNAN (*J. Soc. Chem. Ind.*, 1923, 42, 393—401r).—Examination of soaps with the polarising microscope at magnifications not greater than 100 diameters has revealed the unexpected fact that most soaps are built up of anisotropic material. The typical structures which can be recognised in a soap (the term including pure sodium salts of fatty acids) are: (a) crystals; solid crystals only occur in a few pure sodium soaps, but crystalline fluids, occurring as anisotropic, viscous liquids, syrups or jellies, are general; (b) soap fibres; these may be irregular, tangled masses, of which individual fibres are only faintly anisotropic, or orientated, rope-like or radial structures showing strong double refraction; (c) soap curds, consisting of a mass of fibres entangling a liquid phase; (d) soap gels, which are of infrequent occurrence, and (e) soap solutions. The soap fibres frequently pass when heated into the crystalline fluid form. This phenomenon is observed both in commercial soaps and with pure sodium stearate, palmitate, laurate, and elaidate. The fibres of sodium stearate and elaidate pass into the solid, crystalline form when matured. In each case, the fluid crystals stable at a high temperature revert on cooling into the fibre form. Completely dry fibres do not pass into the fluid, crystalline form when heated. This, and the fact that in presence of salt the fibres do not pass into a crystalline fluid, indicates that the latter is a more highly hydrated phase. Sodium octoate is peculiar in that the crystalline fluid phase is stable at the ordinary temperature. When the dry soap is exposed in a saturated atmosphere the passage of the original grains first into radially grouped fibres and then into a typically crystalline fluid can be observed. In dry air the reverse changes occur.

E. H. R.

**Arachidic Acid, isoBehenic Acid, and n-Eicosanoic Acid.** R. EHRENSTEIN and H. STUEWER (*J. pr. Chem.*, 1923, [ii], 105, 99—207).—isoBehenic acid, formed by the degradation of lignoceric acid (Meyer, Brod, and Soyka, A., 1913, i, 1151), is identical with arachidic acid, obtained from earth-nuts. This acid is not n-eicosanoic acid,  $\text{CH}_3\text{Me}[(\text{CH}_2)_{17}]\cdot\text{CO}_2\text{H}$ , but an isodocosanoic acid,  $_{21}\text{H}_{43}\cdot\text{CO}_2\text{H}$ ; the radicle contained in the latter is also present in lignoceric acid,  $\text{C}_{21}\text{H}_{43}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The acid, m. p. 76—77°, obtained from the oil from *Nephelium Lappaceum*, J. (Baczewski, A., 1896, ii, 209), is n eicosanoic acid, which is also obtained by

p p\*

fusing erucic acid with potassium hydroxide at  $320^{\circ}$ ; its *methylester* forms white, glistening scales, m. p.  $46-47^{\circ}$ , b. p.  $215-216^{\circ}/10$  mm. W. S. N.

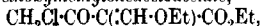
**Erucic and Brassidic Acids and their Anhydrides.** D. HOLDE and F. ZADEK (*Ber.*, 1923, 56, [B], 2052-2058).—An attempt has been made to place beyond doubt the stereochemical relationship of erucic to brassidic acid.

The electrolytic conductivities of the acids and their anhydrides in very highly purified acetone have been measured. The constants of the substances employed are as follows: erucic acid, m. p.  $35.5^{\circ}$ ; erucic anhydride, m. p.  $47.5-48^{\circ}$ ,  $n_D^{20}$  1.4377; iodine number, 76.7; brassidic acid, m. p.  $61.5^{\circ}$  (corr.),  $n_D^{20}$  1.4347; brassidic anhydride, m. p.  $63.5-64.5^{\circ}$ ; iodine number, 76.3. The conductivity of the acetone is  $\kappa=1.01 \times 10^{-7}$ . The conductivities of erucic acid and its anhydride are identical, whereas brassidic anhydride conducts rather better than brassidic acid. The conductivity of the brassidic compounds is noticeably higher than that of the erucic substances. Analogous differences in the conductivities of stereoisomeric substances have been observed with crotonic and isocrotonic acids and with tiglic and angelic acids. From this point of view, erucic acid is related to crotonic and tiglic acids, and brassidic acid to isocrotonic and angelic acids; as judged from the melting point, the relationships are in the inverse order.

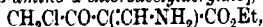
The products obtained by the ozonisation of erucic or brassidic acids are nonaldehyde, b. p.  $80-82^{\circ}/12$  mm.,  $d_4^{20}$  0.893,  $n_D^{20}$  1.4276 (which is further identified as the semicarbazone, m. p.  $83-84^{\circ}$ , and by oxidation to pelargonic acid), and the semialdehyde of brassylic acid which is characterised as the *ethyl ester acetel*,  $C_{19}H_{38}O_4$ , a mobile liquid, b. p.  $175-180^{\circ}/12$  mm., and by oxidation to brassylic acid, m. p.  $109-111^{\circ}$ . The *peroxide* of the semialdehyde of brassylic acid,  $C_{13}H_{24}O_4$ , is described. H. W.

**Ethyl  $\gamma$ -Chloro- and  $\gamma$ -Bromo-ethoxymethyleneacetates and certain Derivatives.** ERICH BENARY and FRANZ EBERT (*Ber.*, 1923, 56, [B], 1897-1900).—The preparation of the substances mentioned in the title is described in detail; the production of cyclic compounds from them has not been effected with certainty.

*Ethyl  $\gamma$ -chloro- $\alpha$ -ethoxymethyleneacetate,*



slender, colourless needles, m. p.  $98^{\circ}$ , b. p.  $160-165^{\circ}/13$  mm., is prepared by the action of orthoformic ester and acetic anhydride on ethyl  $\gamma$ -chloroacetate: the *copper* derivative is described. The ester is rapidly hydrolysed by warm water to *ethyl  $\gamma$ -chloro- $\alpha$ -hydroxymethyleneacetate*, large prisms, m. p.  $18-19^{\circ}$ , b. p.  $131^{\circ}/12$  mm. (*copper* derivative, cornflower-blue platelets, decomp. about  $156^{\circ}$  after previous darkening). The hydroxy-ester is converted by successive treatment with phosphorus trichloride and ice-cold aqueous ammonia into *ethyl  $\gamma$ -chloro- $\alpha$ -aminomethyleneacetate* [*ethyl  $\beta$ -amino- $\alpha$ -chloroacrylate*],



needles, m. p.  $106^{\circ}$ , and by methylamine into *ethyl  $\gamma$ -chloro- $\alpha$ -methyl-aminomethyleneacetate*,  $C_8H_{11}O_2NCl$ , needles, m. p.  $105^{\circ}$ . The latter ester is converted by alcoholic potassium hydroxide or ammonia into solutions which give the pine shaving reaction, but from which only black, decomposed products could be isolated. Treatment of it with sodium hydrogen sulphide in absolute alcohol yields  $\alpha$ -methylaminomethylenethiotetronic acid,  $C_6H_7O_2NS$ , needles, m. p.  $188-189^{\circ}$ .

*Ethyl  $\gamma$ -bromo- $\alpha$ -ethoxymethyleneacetate* forms colourless needles, m. p.  $85^{\circ}$  (copper derivative, lustrous, cornflower-blue leaflets, decomp. about  $152^{\circ}$  after previous darkening). It is very readily hydrolysed to the corresponding *hydroxymethylene* compound, a colourless liquid, which is converted by aqueous ammonia into the compound,  $C_{12}H_{14}O_6N_2$ , lustrous, golden-yellow needles, m. p.  $208-209^{\circ}$  (decomp.). *Ethyl  $\gamma$ -bromo- $\alpha$ -aminomethyleneacetate* crystallises in needles, m. p.  $73^{\circ}$ .

H. W.

**Dissociation Constants of Polybasic Acids and their Application to the Calculation of Molecular Dimensions.** NIELS BJERRUM (*Z. physikal. Chem.*, 1923, **106**, 219-242).—A theoretical paper in which the author discusses the relationships between the values of the ionisation constants of di- and poly-basic acids. The author deals particularly with the influence of the distance between carboxyl groups on the value of the ionisation constants.

J. F. S.

**Esterification of Oxalic Acid.** PAVITRA KUMAR DUTT (T., 1923, **123**, 2714-2715).

**The Relative Stability of Open-chain Dibasic Acids containing Odd and Even Numbers of Carbon Atoms.** WILLIAM ARTHUR PERCIVAL CHALLENGER and JOCELYN FIELD THORPE (T., 1923, **123**, 2480-2485).

**Muconic and Hydromuconic Acids. II. The Isomerism of the Muconic Acids.** ERNEST HAROLD FARMER (T., 1923, **123**, 2531-2548).

**Chemistry of the Sugars. V.** H. KILIANI (*Ber.*, 1923, **56**, [B], 2016-2024; cf. A., 1921, i, 304; 1922, i, 223, 321, 1111).—The removal of the excess of nitric acid left after the oxidation of the sugars by the author's process is relatively seldom so completely effected by the use of ether that the "uronic" or ketonic acids can be isolated by direct crystallisation. They must therefore be converted into derivatives. For this purpose phenylhydrazine and *p*-nitrophenylhydrazine are unsuitable, since they react slowly and do not yield crystalline precipitates. Under definite conditions (which are fully described in the original communication), semicarbazide hydrochloride is very suitable. Somewhat unexpectedly, it is found to give only semicarbazones, instead of semicarbazone-semicarbazide salts. The quantity employed can be based on an expected yield of oxidised product corresponding\* with 30-40% of that theoretically possible. Fission of the semicarbazones is

$p p^* 2$

conveniently effected by oxalic but not by hydrochloric or sulphuric acids. The difficulty of separating the "uronic" or ketonic acids from semicarbazide oxalate has not been completely overcome. The following examples of the new method are cited: conversion of *d*-galactonic into *l*-galacturonic acid [the semicarbazone of *l*-galacturonolactone,  $C_7H_{11}O_6N_3 \cdot H_2O$ , has m. p.  $190^\circ$  (decomp.)]; the oxidation of *l*-mannonic acid into *l*-mannuronic acid [the semicarbazone of *l*-mannuronolactone has m. p.  $189^\circ$  (decomp.) after darkening at  $180^\circ$ ]; the oxidation of  $\alpha$ -glucoheptonic acid and of isosaccharin.

It has been observed incidentally that the sodium salt of the lactone of *d*-saccharic acid can readily be caused to crystallise. Attempts have therefore been made to prepare the analogous potassium salt, which, however, crystallises with extreme difficulty or not at all, whilst, further, its presence greatly hampers the separation of potassium hydrogen *d*-saccharate. It therefore appears that all previous methods of preparing saccharic acid by the aid of the potassium hydrogen salt are subject to error, as is also the customary crystallisation of this salt from boiling water, since it undergoes partial conversion into the salt of the lactonic acid.

H. W.

**Preparation of Chloroacetaldehydesulphonic Acid.** CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 362744; from *Chem. Zentr.*, 1923, ii, 1246).—Dichloroethylene is treated with fuming sulphuric acid, when the following reactions take place:  $CHCl:CHCl + H_2S_2O_7 = SO_3H \cdot CHCl \cdot CHSO_3H + HCl$ ;  $SO_3H \cdot CHCl \cdot CHSO_3H + H_2O = SO_3H \cdot CHCl \cdot CHO + H_2SO_4$ . Ice is added to the products of reaction. The solution is neutralised with sodium carbonate and evaporated in a vacuum. The residue is extracted with hot ethyl alcohol. After removal of the ethyl alcohol by distillation, sodium chloroacetaldehydesulphonate semiacetal,  $SO_3Na \cdot CHCl \cdot CH(OH) \cdot OEt$ , remains. Chloroacetaldehydesulphonic acid and its sodium salt are very hygroscopic. With phenylhydrazine, both the semiacetal and the sulphonic acid give glyoxalbisphenylhydrazone. On heating the sulphonic acid with 80% sulphuric acid, chloroacetaldehyde is obtained. G. W. R.

**The Ketonic Decomposition of Methyl Ethyl Ketone.** CHARLES DEWITT HURD and CYRIL KOCOUR (*J. Amer. Chem. Soc.*, 1923, 45, 2167—2171; cf. Hurd and Cochran, this vol., i, 312).—When methyl ethyl ketone is passed through a tube at  $600^\circ$ , keten (identified by the formation of acetanilide by treating the vapour with anhydrous ethereal aniline) is formed in small yield,  $COMeEt = CH_2CO + C_2H_6$ . Methylketen is apparently not produced,  $COMeEt = CHMeCO + CH_4$ . It is shown that keten reacts much more slowly with water than with aniline or toluidine. W. S. N.

**Calorimetric Study of the Hydrolysis of Ketone Acetals by Water in the Presence of Acids.** L. N. PARFENTIEV (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 455—461).—The hydrolysis of dimethylacetal by water in the presence of traces of the halogen acids or of

sulphuric acid was carried out in a Berthelot calorimeter and the thermal effect was found to be  $-5028$  cal. Water alone does not effect hydrolysis; the catalytic effect of sulphuric acid is only two-fifths of that of the halogen acids; the velocity of the reaction is proportional to the amount of catalyst present. A few experiments with the acetals of methyl ethyl- and methyl butyl-ketones show that the above statements apply also in these cases; the velocity of the reaction appears to diminish with increasing complexity of the substance.

G. A. R. K.

**The Acetals of Saturated Aliphatic Ketones.** V. V. EVLAMPIEV (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 462—465).—Acetals were prepared from several ketones, using ethyl orthoformate in the presence of small quantities of sulphuric acid. It was found that the optimum amount of catalyst was not the same in all cases; the velocity of the reaction diminishes with increasing molecular weight and is greater in normal than in *iso*-compounds. No acetal could be obtained from pinacolin whilst methyl hexyl ketone reacted readily, but the product was a *compound*,  $C_{10}H_{20}O$ , b. p.  $71.9^{\circ}/10$  mm.,  $d^{20}_D$  0.8232,  $d^{20}_D$  0.8075, which was formed from the acetal by the loss of a molecule of ethyl alcohol. The *diethyl acetals* of the following ketones were prepared: of methyl ethyl ketone, b. p.  $59.2^{\circ}/43$  mm.,  $d^{20}_D$  0.8586,  $d^{20}_D$  0.8416; of methyl propyl ketone, b. p.  $57.4^{\circ}/18.5$  mm.,  $d^{20}_D$  0.8574,  $d^{20}_D$  0.8409; of methyl isopropyl ketone, b. p.  $52.4^{\circ}/20$  mm.,  $d^{20}_D$  0.8627,  $d^{20}_D$  0.8453; of methyl butyl ketone, b. p.  $78.7^{\circ}/23.5$  mm.,  $d^{20}_D$  0.8573,  $d^{20}_D$  0.8414; of ethyl propyl ketone, b. p.  $74.8^{\circ}/18.5$  mm.,  $d^{20}_D$  0.8624,  $d^{20}_D$  0.8470; of methyl isobutyl ketone, b. p.  $72.4^{\circ}/18$  mm.,  $d^{20}_D$  0.8559,  $d^{20}_D$  0.8396; of dipropyl ketone, b. p.  $76.5^{\circ}/12$  mm.,  $d^{20}_D$  0.8577,  $d^{20}_D$  0.8422.

G. A. R. K.

**Pentosans. V. Hydrolysis of Xylan by Means of Dilute Nitric Acid.** EMIL HEUSER and GEORG JAYME (*J. pr. Chem.*, 1923, [ii], 105, 232—241).—The method for preparing xylose by hydrolysing xylan by means of dilute mineral acids (Heuser and Brunner, this vol., i, 184) has now been improved by using 3% nitric acid, and continuing the process for one hour. The product is colourless, and readily crystallises; the yield is 85% of the theoretical, and furfuraldehyde is not formed. The modified process is thus quicker and more economical. The conditions giving the best yield of xylose are also those for which the amount of sugar formed, as estimated by Bertrand's reduction method (*loc. cit.*), is a maximum (97.04% theory). It is remarkable that xylan passes completely into solution after being warmed for one to two minutes with 45 times its weight of 3% nitric acid at  $100^{\circ}$ . At this stage, according to the "reduction" estimation, 58.72% of xylose is already produced, but xylose is not obtained from the solution. Instead, a colloidal substance, resembling dextrin, undoubtedly a "xylo-dextrin," is obtained.

W. S. N.

**Pentosans. VI. Oxidation of Xylan by Means of Nitric Acid.** EMIL HEUSER and GEORG JAYME (*J. pr. Chem.*, 1923, [ii], 105, 283—287).—E. Fischer has obtained trihydroxyglutaric acid

(A., 1891, 1173) by oxidising xylose by means of nitric acid, *d* 1.2. Hence xylan, which is hydrolysed to xylose by the action of nitric acid (cf. preceding abstract), should give the same product. This prediction is verified. Xylan is dissolved in two and a half times its weight of nitric acid, *d* 1.2, at 70°, and the solution kept at 45°. The yield, as the calcium salt, is 21.71% of the theoretical. If twice the above quantity of nitric acid is used, only a small quantity of trihydroxyglutaric acid is formed, together with much oxalic acid.

W. S. N.

**The Isolation from Cabbage Leaves of a Carbohydrate hitherto undescribed containing three Carbon Atoms.**

HAROLD WILLIAM BUSTON and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1923, 17, 470—472).—The carbohydrate has the formula  $C_3H_5O_4$ . It crystallises in needles, m. p. 148°, which are soluble in cold water and hot glacial acetic acid, but insoluble in most other organic solvents. A tribenzoyl derivative,  $C_3H_3O_4Bz_3$ , m. p. 52—53°, was obtained from it. It is assumed, therefore, that the carbohydrate has the constitution  $OH\cdot CH_2\cdot CH(OH)\cdot O\cdot CH_2\cdot OH$ . The possible origin of the compound and its contribution to the formation of the anthocyanins in the plant are discussed. S. S. Z.

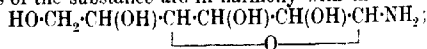
**Observations on the Mutarotation of Dextrose in Aqueous-Alcoholic Solutions.**

HANS VON EULER and ELSA ERIKSON (*Biochem. Z.*, 1923, 140, 263—272).—The mutarotation constants of dextrose were measured at  $p_H$  3.0, using phosphate and citrate buffers in the presence of increasing percentage volumes of alcohol from 0 to 50%. The constants steadily diminished with increasing concentrations of alcohol, more especially in the presence of citrates. From the nature of the results, it is concluded that the inactivation of invertase in the presence of alcohol is not due to steric alterations of the substrate.

J. P.

**A Compound of Dextrose with Ammonia.**

A. SCHMUCK (*Ber.*, 1923, 56, [B], 1817—1819).—The action of gaseous ammonia on an alcoholic solution of dextrose leads to the production of a substance which has been designated glucosimine by Lobry de Bruyn. Further examination of the substance has shown that it readily reacts with nitrous acid with evolution of nitrogen, and hence contains the primary amino-group, whilst, also, the difficulty with which it is transformed into a pyrrole derivative indicates the absence of a ring containing nitrogen; it is converted by benzoyl chloride and aqueous sodium hydroxide into a *heptabenzoyl*,  $C_6H_5O_6NBz_7$ , m. p. 91°, which gives a *nitroso*-derivative. The reactions of the substance are in harmony with the formula



the name *isoglucosamine* is proposed.

H. W.

**Sources of the Rare Sugars. VIII. Preparation of Lævulose.**

T. SWANN HARDING (*Sugar*, 1923, 406—408; cf. A., 1922, i, 919).—A solution containing 250 g. of granulated sucrose is treated with invertase, concentrated in a vacuum to 85% solids, "seeded"

with dextrose, and set aside in a cool place. Sufficient ethyl alcohol is added to the mass of crystals to render it mobile, following which the dextrose is separated by centrifuging, the yield being about 25% of the sucrose taken. After distilling off the alcohol, the mother-liquor is diluted to 1,500 c.c., cooled to  $5-10^{\circ}$ , and treated with 115 g. of calcium oxide, previously slaked and cooled to at least  $10^{\circ}$ , the mixture being vigorously stirred for five minutes. The resulting calcium lævulosate is separated as quickly as possible by centrifuging, washed with iced lime-water, thrown into iced water, and the mixture neutralised with dilute sulphuric acid (25%). After filtering off the calcium sulphate, the solution is evaporated in a vacuum to a thick syrup, treated with two volumes of ethyl alcohol to precipitate the salts, a little decolorising carbon added, and the mixture set aside over-night. It is filtered, and concentrated in a vacuum to a syrup of 90–95% solids, from which the lævulose may be crystallised after the addition of alcohol containing nitric acid, the yield being 20–22% of the weight of sucrose taken. A further yield of dextrose may be obtained from the liquor from the centrifuging of the calcium lævulosate (which should meanwhile have been kept at a low temperature) by neutralising with dilute sulphuric acid, filtering, concentrating to a thin syrup, refiltering, continuing the concentration to a thick syrup, and adding ethyl alcohol containing 1% of nitric acid, the yield of the crystals thus obtained being about 15% of the sucrose employed.

J. P. O.

**The Fission of Methylated Lactose.** HANS HEINRICH SCHLUBACH and KARL MOOG (*Ber.*, 1923, 56, [B], 1957–1963).—It has been shown by Haworth and Leitch (*T.*, 1918, 113, 188) that heptamethyl- $\beta$ -methyl-lactoside is hydrolysed by aqueous hydrochloric acid to 2:3:5:6-tetramethylgalactose and 2:3:6-trimethylglucose. The authors have expressed the opinion that the operation occurs in two stages, involving first the rupture of the disaccharide linking and then of the methylglucoside union. This hypothesis is now confirmed by the isolation of 2:3:6-trimethyl- $\beta$ -methylglucoside as hydrolytic product.

The optimal conditions for the hydrolysis of heptamethyl- $\beta$ -lactoside, m. p.  $81.5-82^{\circ}$ ,  $n_D^{20}$  1.4642,  $[\alpha]_D^{17} -1.62^{\circ}$  in water for  $c=0.924$  (Haworth and Leitch give m. p.  $77-82^{\circ}$ ,  $n_D^{20}$  1.4675,  $[\alpha]_D^{10} +5.19^{\circ}$  for  $c=0.771$ ), are established by preliminary kinetic measurements of the velocity of hydrolysis of the substance and of trimethyl- $\beta$ -methylglucoside by aqueous hydrochloric acid. After hydrolysis, the tetramethylgalactose is removed as the anilide and trimethyl- $\beta$ -methylglucoside is isolated from the residual oil by distillation (cf. Haworth and Leitch, *loc. cit.*); since, however, the production of the anilide is not quantitative and is strongly influenced by unknown factors (cf. Irvine and Hirst, *T.*, 1922, 121, 1213), the yields of trimethyl- $\beta$ -methylglucoside are very variable.

[With HELMUT FIRGAU.]—The isolation of trimethyl- $\beta$ -methylglucoside is more readily affected when heptamethyl- $\beta$ -methyl-

lactoside is hydrolysed with methyl-alcoholic hydrogen chloride (1%) at 100°. The product consists of a mixture of tetramethyl- $\alpha$ - and  $\beta$ -methylgalactosides with trimethyl- $\beta$ -methylglucoside, which cannot be separated into its components by fractional distillation. It is therefore treated with benzoyl chloride in the presence of pyridine, whereby the glucoside is converted into its benzoyl derivative, which differs by about 40° in boiling point from the galactosides. The glucoside is quantitatively regenerated from its benzoyl compound by means of alcoholic potassium hydroxide solution.

2:3:6-Trimethyl- $\beta$ -methylglucoside crystallises in long needles, m. p. 60.5°, b. p. 81°/0.04 mm.,  $n_D^{20}$  1.4548,  $[\alpha]_D^{20}$  -34.60° (c=0.9908). 5-Benzoyl-2:3:6-trimethyl- $\beta$ -methylglucoside has b. p. 134—135°/0.08 mm.,  $n_D^{20}$  1.5020—1.5028,  $[\alpha]_D^{20}$  -23.87° in aqueous alcoholic solution (50%) for c=0.5654. 5-Acetyl-2:3:6-trimethyl- $\beta$ -methylglucoside, b. p. 106°/0.055 mm.,  $[\alpha]_D^{20}$  -14.17° in water (c=1.2352), is prepared from the glucoside and acetic anhydride in the presence of pyridine. 2:3:5:6-Tetramethyl- $\beta$ -methylgalactoside has m. p. 48—48.5°, b. p. 87°/0.035 mm.,  $n_D^{20}$  1.4420,  $[\alpha]_D^{20}$  +19.59° in aqueous solution for c=0.9872 [Irvine and Cameron (T., 1904, 85, 1073), give m. p. 44—45°,  $[\alpha]_D$  +30.7°, for c=4.968]. 2:3:5:6-Tetramethyl- $\alpha$ -galactose, obtained by hydrolysis of the corresponding  $\beta$ -methylgalactoside or of the anilide, forms well-defined crystals, m. p. 71.5—72°, b. p. 96°/0.01 mm.,  $n_D^{20}$  1.4622,  $[\alpha]_D^{20}$  +142.0°  $\rightarrow$  118.0°. H. W.

**Sources of the Rare Sugars. IX. (Preparation of Trehalose.)** T. SWANN HARDING (*Sugar*, 1923, 476—478).—About 500 g. of trehala manna are extracted with 2,500 c.c. of 75% alcohol during two hours, using a reflux condenser, after which the operation is repeated with 750 c.c. The two extracts are united, filtered, concentrated to 400 c.c., diluted with 1,000 c.c. of water, and clarified by the addition of basic lead acetate, the excess of which after filtering is eliminated by precipitation as sulphide. On evaporating the filtrate to 100 c.c., and adding about 50 c.c. of 95% ethyl alcohol, crystallisation proceeds rapidly, more alcohol being added from time to time to prevent the formation of a solid cake. A yield of 20—25% is given by this method. A procedure using *Selaginella lepidophylla* ("resurrection plant") as raw material is also described, but in this case the yield is only 1—1.5%. Previous work done on the preparation of this sugar is summarised.

J. P. O.

**Studies on Starch. I. The Nature of Polymerised Amylose and of Amylopectin.** ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (T., 1923, 123, 2666—2688).

**Soluble Esters of Starch with the Higher Fatty Acids.** H. GAULT (*Compt. rend.*, 1923, 177, 592—593; cf. this vol., i, 757).—When starch is heated with lauryl chloride in presence of pyridine and (as solvent) toluene, starch dilaurate,  $C_6H_5O_3(CO_2C_{11}H_{23})_2$ , is obtained, in 80% yield, as scaly material, m. p. 130°, insoluble in hydroxylic and soluble in non-hydroxylic solvents. E. E. T.

**The Action of Light on Cotton. A Summary of the Literature.** PERCY W. CUNLIFFE (*J. Text. Inst.*, 1923, **14**, 314—318r).—The scanty literature dealing with the photochemistry of cotton is reviewed. It is not yet clear what part light plays in the deterioration of cotton fabrics apart from activating the surrounding atmosphere.  
J. C. W.

**The Swelling of Cotton Cellulose. A Summary of the Literature.** GEORGE ERNEST COLLINS (*J. Text. Inst.*, 1923, **14**, 264—276r).—Two hundred papers dealing with the swelling of cotton cellulose in water, and in solutions of acids, alkalis, and salts, are summarised.  
J. C. W.

**Swelling of Cotton Cellulose. I. Cotton Hairs in Solutions of Sodium Hydroxide.** GEORGE ERNEST COLLINS and ALEXANDER MITCHELL WILLIAMS (*J. Text. Inst.*, 1923, **14**, 287—295r).—Observations have been taken of the change in length, mean diameter, and number of convolutions per centimetre of single cotton hairs on immersion in water and in solutions of sodium hydroxide. For changes in length, a delicate instrument reading to 0.01 mm., modelled on Justin-Mueller's turgometer, was used. Diameters and convolution numbers were determined by direct observation in a glass cell mounted on the stage of a horizontal microscope fitted with a micrometer; polarised light was used, and the hairs appeared alternately red and green, especially in 9% sodium hydroxide, indicating frequent reversals of optical activity in the material. The technique and results are fully described.

It is found that the increase in length which is observed on immersion in water is due almost entirely to the straightening out of convolutions. Maximum swelling occurs in a 14.5% solution of sodium hydroxide, and hairs which have been immersed in solutions up to the highest concentration used (48%), on transference to more dilute solutions, also swell to the maximum extent in 15% alkali.

In one experiment, the cotton hairs were taken through solutions of sodium hydroxide up to 48%, then back through dilute solutions to water, and finally through hydrochloric acid of increasing concentration. Maximum extension, and presumably minimum swelling, occurred with 10% hydrochloric acid. Cotton cellulose appears, therefore, to be analogous to a heavy metallic hydroxide of definite acidic character; the point of maximum swelling (14.5% NaOH) corresponds with a point of maximum solubility, the reduction in swelling in more concentrated alkali with reduced solubility because of the repressed ionisation of the salt, the absence of swelling in acid with insolubility of the solid acid, and the minimum swelling in 10% hydrochloric acid with an isoelectric point.  
J. C. W.

**The Mercerisation of Cotton. A Review of the Literature.** DOUGLAS ARTHUR CLIBBENS (*J. Text. Inst.*, 1923, **14**, 217—249r).—A critical summary, with seventy-nine references to the literature,

dealing with mercerisation under the following headings: history, microscopic characteristics of mercerised cotton, lustre of cotton mercerised under tension, shrinkage of cotton when treated with sodium hydroxide, tensile strength of mercerised cotton, reactivity and adsorptive capacity of mercerised cotton, nature of mercerised cotton and the mercerisation process, and tests for mercerised cotton. J. C. W.

**The Hemicelluloses. I. The Hemicellulose of Wheat Flour.** DONALD HERBERT FRANK CLAYSON and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1923, 17, 493—496).—By removing from wheat flour the gliadin with 70% alcohol, the starch by the action of taka-diaxase, and the glutenin by extraction with 0.1% sodium hydroxide a hemicellulose is obtained. The compound is soluble in hot water, from which it separates in an amorphous form. It is also soluble in N-sodium hydroxide and is precipitated on the addition of acids. The pure compound, precipitated from hot water or obtained from the copper salt, has  $[\alpha]_D^{20} + 150^\circ$  in 0.5N-sodium hydroxide. It is not an intermediate product in the digestion of the starch by taka-diaxase. S. S. Z.

**The Hemicelluloses. II. The Hemicellulose Content of Starch.** SAMUEL BARNETT SCHRYVER and ETHEL MARY THOMAS (*Biochem. J.*, 1923, 17, 497—500).—Employing the same method of extraction (see preceding abstract), hemicellulose was obtained from the starches of sago, maize, wheat, rice, tapioca, and potato. The yields varied practically from 0 in the case of potato starch up to nearly 4% in that of sago. The compound has a composition which corresponds with the formula  $C_{18}H_{34}O_{17}$  ( $=3C_6H_{10}O_5 \cdot 2H_2O$ ), and yields, on hydrolysis, dextrose as the only reducing sugar, mixed with small amounts of other products, probably of a dextrin-like nature. S. S. Z.

**The Hemicelluloses. III. The Hemicellulose of American White Oak.** MARGARET HELENA O'DWYER (*Biochem. J.*, 1923, 17, 501—509).—The hemicellulose was prepared by extracting the washed sawdust with 4% sodium hydroxide and precipitating the extract with acetic acid. A rough quantitative estimation of the products of hydrolysis showed the presence of 51.5% of xylose, and 18.5% of arabinose; the remaining 30% consisted of mannose and galactose. Untrustworthy figures were obtained in the estimation of the relative quantities of mannose and galactose. S. S. Z.

**Hydrochloric Acid-Lignin.** ERIK HÄGGLUND (*Ber.*, 1923, 56, [B], 1866—1868).—Pine wood is readily attacked by hydrochloric acid (45%) at 0°, leaving a residue of hydrochloric acid-lignin. The latter substance can be further hydrolysed by treatment with boiling dilute hydrochloric or sulphuric acid, and the residue from this operation is again susceptible to treatment with the cold concentrated acid. It is not yet established whether complete solution of the lignin can be obtained by repeated alternate treatments. The pentoses (chiefly arabinose) formed by hydrolysis correspond approximately with half the loss in weight

of the lignin. It is probable that methylpentoses are also present, since the furfuraldehyde distillates of the residues contain appreciable quantities of methylfurfuraldehyde.

H. W.

**Lignin. IV. The Oxidation of Alkali Lignins by Hydrogen Peroxide.** OTTO ANDERZÉN and BROR HOLMBERG (*Ber.*, 1923, 56, [B], 2044—2048; cf. Holmberg and Wintzell, A., 1921, i, 850).

The oxidation of  $\alpha$ - or  $\gamma$ -lignin by hydrogen peroxide in the presence of water yields formic, acetic, oxalic, malonic, and succinic acids. The formation of the latter acid is somewhat remarkable, but is in harmony with the assumption that the coniferyl or vanillyl residue is a component of the lignin molecule. It may be obtained by the oxidation of vanillin. The oxidation of alkali lignins in alkaline solution leads to the production of oxalic, formic, and acetic acids, the yield of the latter not exceeding 1—1.6%. Since yields of 7—10.5% of the latter acid are obtained by the oxidation of hot, acid solutions, it appears that a portion of it is derived from primarily formed malonic acid.

H. W.

**Pectin-Sugar-Acid Gels.** R. SUCHARIPA (*J. Assoc. Off. Agric. Chem.*, 1923, 7, 57—68).—Gels may be prepared by adding 5 g. of 4% pectin solution to 15 g. of 75% sucrose syrup containing 0.75% of citric acid; heating does not accelerate the setting of such gels, low temperature and evaporation being the promoting factors. The formation of such gels is due to the coagulation of pectin in the sucrose-acid medium. Pectin is very slightly soluble in sucrose-acid solutions. The mother-liquor separates from even very tough jellies, although in smaller amount than from soft jellies; the solid (after washing with alcohol) contains pectin only, whilst the liquid part contains all the acid, sugar, traces of pectin, and a small amount of methyl alcohol. The cleavage of methoxyl groups is, however, of very limited extent, since the recovered pectin will again form good gels. Pectins with different methoxyl contents have been prepared; they yield solutions of varying viscosity, and the gels prepared with them increase in strength with increase in the methoxyl content. The jelly-forming property of pectin is destroyed by prolonged heating, high temperature, and pressure.

W. P. S.

**Syntheses from Hydrocyanic Acid by Means of the Silent Discharge. III. Behaviour of Amylene.** L. FRANCESCONI and A. CIURLO (*Gazzetta*, 1923, 53, 521—522; and *Atti R. Accad. Lincei*, 1923, [v], 32, ii, 34—35).—Like other hydrocarbons (this vol., i, 764, 1004), amylene reacts with hydrocyanic acid under the influence of the silent discharge, yielding nitrile and isonitrile compounds in fluctuating proportions.

T. H. P.

**Synthesis of Amines by Means of the Silent Discharge. I.** L. FRANCESCONI and A. CIURLO (*Gazzetta*, 1923, 53, 598—600; cf. this vol., i, 764, 1004, and preceding abstract).—The action of the silent discharge on a mixture of dry ethylene and ammonia in an ordinary Berthelot ozoniser at the ordinary temperature results in the formation of ethylamine in about 10% yield with reference

to the ethylene, and of an oily product (cf. Losanitsch, A., 1908, ii, 32). T. H. P.

**The Ammonium Radicle. IV. Tetraethylammonium.**  
**III. The Similarity to the Alkali Metals.** HANS HEINRICH SCHLUBACH and GUSTAV VON ZWEHL (*Ber.*, 1923, 56, [B], 1889—1892).—A continuation of previous work (Schlubach and Ballauf, A., 1922, i, 15). Solutions of tetraethylammonium in liquid ammonia have been prepared under conditions so modified as to exclude the possibility of contamination with alkali metals. The colorations given by these solutions with organic substances containing unsaturated bonds (benzophenone, phenyl diphenyl ketone, dimethylpyrone,  $\beta$ -benzpinacolin, benzil, phenanthraquinone, anthracene, stilbene, tetraphenylethylene, benzylideneaniline, azobenzene, tolane, toluonitrile) are described in detail, and are shown to be closely similar to those given by these compounds with the alkali metals. Tetraethylammonium appears, therefore, to function as a true pseudo-metal. H. W.

**The Ammonium Radicle. V. Onium Radicles.** HANS HEINRICH SCHLUBACH and HERMANN MIEDEL (*Ber.*, 1923, 56, [B], 1892—1896).—An examination of the influence of substituents on the stability of the ammonium radicle and of the possible existence of radicles which contain a central atom other than nitrogen.

The substituted ammonium salts are submitted to electrolysis, liquid ammonia being used as solvent. The formation of a radicle is indicated by the production of a blue colour in the solution, or, more accurately, by the development of a coloration in the presence of 2 : 6-dimethylpyrone.

For the formation of ammonium radicles, it appears necessary that an alkyl group should be attached to the nitrogen atom. Successive replacement of the ethyl groups of tetraethylammonium by benzyl radicles increases the instability of the ammonium complex; the effect is still more pronounced when the triphenylmethyl or phenyl group takes the place of benzyl. Instability is also conferred on the substituted ammonium radicle when the ethyl group is replaced by hydrogen.

Electrolysis of tetraethylphosphonium and tetraethylarsonium iodides dissolved in liquid ammonia gives rise to radicles which do not cause the solution to become blue, but are detected by the colorations given with 2 : 6-dimethylpyrone. Diphenyliodonium iodide, under similar conditions, does not appear to give a radicle.

It appears, therefore, that a large class of complexes exists, to which the name "onium radicles" is assigned, owing to their preparation from onium salts. These differ from the usual radicles in that the valency of the central atom is greater by one unit than that observed in the stable hydrogen compound of the atom, whereas in the usual radicles it is less by one unit. H. W.

**The Preparation of  $\beta$ -Methylhydroxylamine by the Aid of Potassium Hydroxylamineisodisulphonate.** WILHELM TRACKE and ALFRED P. SCHULZ (*Ber.*, 1923, 56, [B], 1856—1860).—The recent investigations of Raschig (this vol., ii, 161) on the preparation

potassium hydroxylamineisodisulphonate,  $\text{SO}_3\text{K}\cdot\text{NH}\cdot\text{O}\cdot\text{SO}_3\text{K}$ , are rendered possible the convenient preparation of  $\beta$ -methylhydroxylamine.

Potassium hydroxylamineisodisulphonate is dissolved in rather more than the quantity of aqueous potassium hydroxide solution which is theoretically necessary for the production of the basic salt, and the solution is treated with methyl sulphate or methyl iodide, whereby potassium  $\beta$ -methylhydroxylamineisodisulphonate,  $\text{O}_2\text{K}\cdot\text{NMe}\cdot\text{O}\cdot\text{SO}_3\text{K}$ , minute rhombohedra, is readily obtained; the corresponding silver, lead, and barium salts are described. The isolation of the potassium salt is not necessary for the preparation of  $\beta$ -methylhydroxylamine, for which purpose the solution is treated with acid. The direct isolation of  $\beta$ -methylhydroxylamine in the form of one of its salts from the resulting solution does not appear to be practicable. The solution is therefore rendered slightly alkaline and treated with successive small quantities of benzaldehyde, care being taken to maintain the alkalinity by periodical additions of potassium hydroxide. It is filtered through wet paper, and the *N*-methylbenzaldoxime is extracted from the filtrate by chloroform. The oxime is purified and subsequently decomposed by hydrochloric, sulphuric, or oxalic acid. The yield of  $\beta$ -methylhydroxylamine hydrochloride, calculated on the hydroxylamineisodisulphonate taken, is 60–70% of that theoretically possible.

The following salts of  $\beta$ -methylhydroxylamine are described; the hydrochloride, very hygroscopic crystals, m. p.  $87^\circ$ ; the normal malate,  $2\text{CH}_3\text{ON}\cdot\text{H}_2\text{C}_2\text{O}_4$ , long needles, m. p.  $159^\circ$ ; the hygroscopic, normal sulphate, m. p.  $130^\circ$ ; the picrate, m. p.  $268^\circ$ . H. W.

#### Synthesis of $\gamma$ -Aminobutyric Acid from Ethyl Glutaryl-aminoacetate.

THEODOR CURTIUS and WILHELM HECHTENBERG. *J. pr. Chem.*, 1923, [ii], **105**, 319–326).—Glutaryl chloride and ethyl aminoacetate hydrochloride react in boiling benzene solution to give the half-chloride,  $\text{COCl}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , a thick, yellow oil, b. p.  $179\text{--}180^\circ/14\text{ mm.}$ , which is converted, on keeping with concentrated aqueous ammonia solution for several days, into the corresponding amide,  $\text{NH}_2\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , glistening, colourless needles, m. p.  $188^\circ$ . The half-chloride reacts vigorously with hydrazine hydrate, giving ethyl hydrazidoglutaryl-aminoacetylhydrazide,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , glistening, colourless leaflets, m. p.  $166^\circ$  (decomp.), dihydrochloride, m. p.  $190^\circ$  (decomp.), dibenzylidene derivative, m. p.  $220^\circ$ . The dihydrazide is converted by treatment with nitrous acid in aqueous solution into the diazide, a thick, colourless, unstable oil, which reacts with alcohol in ethereal solution to give the diurethane, glistening leaflets, m. p.  $143^\circ$ . The latter gives  $\gamma$ -aminobutyric acid (hydrochloride), when hydrolysed by means of concentrated hydrochloric acid at  $100^\circ$ . W. S. N.

#### Resolution of Non-naturally Occurring Amino-Acids and polypeptides. III. EMIL ABDERHALDEN and KIKO GOTO

*fermentforsch.*, 1923, **7**, 95–105).—Ferments are capable of

hydrolysing the amide linking of non-naturally occurring peptides, *dl*- $\alpha$ -Amino-octoic acid was prepared by the action of aqueous ammonia on  $\alpha$ -bromo-octoic acid. It melts at 263–264°. It was converted by the action of chloroacetyl chloride and  $\alpha$ -bromoisohexoyl chloride, respectively, into *chloroacetyl-dl*- $\alpha$ -amino-octoic acid, m. p. 82–83°, and  *$\alpha$ -bromoisohexoyl-dl*- $\alpha$ -amino-octoic acid, m. p. 123°. By the action of alcoholic ammonia these halogenated acids gave the dipeptides, *glycyl-dl*- $\alpha$ -amino-octoic acid, m. p. 196°, and *dl*-leucyl-*dl*- $\alpha$ -amino-octoic acid, m. p. 230°. The hydrochlorides of the *ethyl* and *methyl* esters of  $\alpha$ -amino-octoic acid melt at 53–54° and 76–77°, respectively. The formyl derivative of *dl*- $\alpha$ -amino-octoic acid was resolved by means of brucine, the salt of *d*-formyl-amino-octoic acid separating first, and giving on hydrolysis *l*- $\alpha$ -amino-octoic acid, m. p. 276°, and  $[\alpha] -12.99^\circ$ . From the mother-liquors *d*- $\alpha$ -amino-octoic acid was eventually obtained having  $[\alpha] +12.28^\circ$ . By the action of yeast on *dl*- $\alpha$ -amino-octoic acid, the dextrorotatory component was selectively utilised, leaving a slight preponderance of the *l*-form. The dipeptides *glycyl-dl*- $\alpha$ -amino-octoic acid and *dl*-leucyl-*dl*- $\alpha$ -amino-octoic acid were submitted to the action of yeast press juice with suitable buffering. In the former case *d*- $\alpha$ -amino-octoic acid and glycine were isolated, and in the latter *l*-leucine with a trace of *d*- $\alpha$ -amino-octoic acid.

H. K.

### Resolution of Non-naturally Occurring Racemic Amino-acids by Ferments. III. EMIL ABDERHALDEN and MUNENARI TANAKA (*Fermentforsch.*, 1923, 7, 153–159).— $\alpha$ -Aminomyristic acid was combined with chloroacetyl chloride, yielding *chloro*- $\alpha$ -acetamidomyristic acid, m. p. 205°.

The reaction proceeds better if the ethyl ester (2 molecules) is coupled with chloroacetyl-chloride in chloroform solution. *Ethyl*  $\alpha$ -aminomyristate hydrochloride melts at 83°, the *methyl* ester hydrochloride at 105°, and the *chloroacetyl* derivative of the ethyl ester at 58°. The latter is transformed by alcoholic ammonia at 37° into the dipeptide,  $\alpha$ -glycylamidomyristic acid, m. p. 212°. Under parallel conditions,  $\alpha$ -bromoisohexoyl chloride converts the ethyl ester of  $\alpha$ -aminomyristic acid into *ethyl*  $\alpha$ -bromoisohexoyl- $\alpha$ -amidomyristate, m. p. 44°, which yields *dl*- $\alpha$ -leucylamidomyristic acid, m. p. 218°. This latter acid forms an acid chloride on treatment with thionyl chloride. By the action of yeast on *dl*- $\alpha$ -aminomyristic acid, a weakly levorotatory acid was obtained of doubtful purity. Yeast press juice was allowed to act on the dipeptides mentioned above but with inconclusive results.

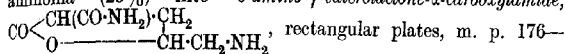
H. K.

**Synthesis of Methyl  $\beta$ -Methylaminopropene- $\alpha$ -carboxylate,  $\text{NHMe}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{Me}$ .** G. KORSCHUN and (MME) C. ROLL (*Bull. Soc. chim.*, 1923, [iv], 33, 1106–1107).—When methyl acetoacetate is agitated with 33% aqueous methylamine in the cold, *methyl*  $\beta$ -methylaminopropene- $\alpha$ -carboxylate, m. p. 60.5°, is formed. It is hydrolysed quantitatively by dilute sulphuric acid, and this reaction may be used for its estimation, provided that

the hydrolysis is carried out without the application of heat (about twenty-four hours are required) to avoid loss of methylamine.

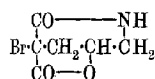
H. H.

**$\alpha$ -Diamino- $\gamma$ -valerolactone and a New Synthesis of Hydroxyproline.** WILHELM TRAUBE, R. JOHOW, and W. TERPOHL (*Ber.*, 1923, 56, [B], 1861—1866; cf. Leuchs, A., 1905, i, 545).—Ethyl chlorovalerolactonecarboxylate is transformed by aqueous ammonia (25%) into  $\delta$ -amino- $\gamma$ -valerolactone- $\alpha$ -carboxylamide,



178°. It is converted by barium hydroxide solution into the corresponding free acid, which could not be obtained in a completely homogeneous condition; its constitution is deduced by its transformation with loss of carbon dioxide into the oxypiperidone, m. p. 144—145°. The aqueous solution of the acid is treated with bromine and subsequently heated until evolution of carbon dioxide ceases, whereby  $\alpha$ -bromo- $\delta$ -amino- $\gamma$ -valerolactone hydrobromide,  $\text{CHBr}\cdot\text{CH}_2 > \text{CH}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HBr}$ , m. p. 215—216°, is obtained. The latter substance is transformed by water and silver oxide into  $\gamma$ -hydroxyproline.

Bromination of aminovalerolactonecarboxylamide dissolved in water or glacial acetic acid leads to the production of the lactone



of 3-bromo-5-hydroxypiperidone-3-carboxylic acid (annexed formula), m. p. 240° (decomp.), which is converted by concentrated alcoholic ammonia into  $\alpha$ -diaminovalerolactonecarboxylamide,  $\text{C}_6\text{H}_{11}\text{O}_3\text{N}_3$ , m. p. 215—220° after becoming changed at 200°. Treatment of the latter substance with sodium hydroxide solution gives an acid,  $\text{C}_6\text{H}_{11}\text{O}_6\text{N}_2$ , needles, m. p. 210—212°, which is either the corresponding carboxylic acid (+2H<sub>2</sub>O), or, possibly,  $\alpha$ -carboxy- $\alpha$ -diamino- $\gamma$ -hydroxyvaleric acid (+H<sub>2</sub>O). When warmed with dilute nitric acid, it

yields  $\alpha$ -diamino- $\gamma$ -valerolactone,  $\text{CH}(\text{NH}_2)\cdot\text{CH}_2 > \text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$ , a

viscous liquid which readily absorbs atmospheric moisture and carbon dioxide; it is characterised as the corresponding nitrate,  $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HNO}_3$ , rectangular plates, m. p. 153—155°, the hydrochloride,  $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HCl}\cdot\text{H}_2\text{O}$ , rhombic plates, m. p. 239—240°, and the carbamide derivative,  $\text{C}_7\text{H}_{12}\text{O}_4\text{N}_4$ , slender needles, m. p. 204—206°.

Ethyl chlorovalerolactonecarboxylate is converted by guanidine in boiling alcoholic solution into the compound,  $\text{C}_7\text{H}_9\text{O}_3\text{N}_3$ , slender needles which have no definite melting point.

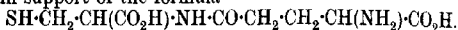
H. W.

**The Fission of Polypeptide Esters by Lipase.** EMIL ABDERHALDEN and ALFRED ÄLKER (*Fermentforsch.*, 1923, 7, 77—84).—Attempts to resolve polypeptides by selective hydrolysis of the esters by lipase were not successful. Glycyl-dl-leucylglycine, prepared by the action at 37° of 25% ammonia on chloroacetyl-

dl-leucylglycine (m. p. 127—137°) decomposes at 227° and gives a weak biuret reaction. Its ethyl ester was amorphous. dl-Leucylglycyl-dl-leucylglycine, m. p. 235°, was prepared by the action of ammonia on dl- $\alpha$ -bromoisohexoylglycyl-dl-leucylglycine, m. p. 195° (decomp.). The former tetrapeptide gave an intense red biuret reaction. Its ethyl ester was amorphous and gave a rose-coloured biuret reaction. Lipase failed to hydrolyse either of these esters.

H. K.

**Glutathione. IV. Constitution.** JUDA HIRSCH QUASTEL, CORBET PAGE STEWART, and HUBERT ERLIN TUNNICLIFFE (*Biochem. J.*, 1923, **17**, 586—592).—The following evidence is produced in support of the formula

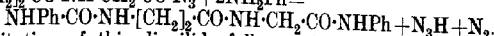


When the free amino-group of the compound is condensed with 2:3:4-trinitrotoluene, the resulting compound on hydrolysis yields cysteine, but not free glutamic acid. On replacing the free amino-group of glutathione by a hydroxyl group,  $\alpha$ -hydroxy-glutaric acid is obtained on hydrolysis. Oxidation of glutathione by hydrogen peroxide yields succinic acid only after hydrolysis of the oxidation product, thus demonstrating which carboxyl group of glutamic acid is condensed with the amino-group of cysteine.

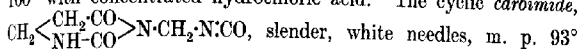
S. S. Z.

**Synthesis of  $\beta$ -Alanine from Ethyl Succinylamidoacetate.** THEODOR CURTIUS and WILHELM HECHTENBERG (*J. pr. Chem.*, 1923, [ii], **105**, 289—318).—The action of an excess of hydrazine hydrate on ethyl succinylamidoacetate gives *hydrazidosuccinylglycinehydrazine*,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , colourless, anisotropic tablets, m. p. 167° (decomp.). If the materials are not well cooled during the reaction, a compound, m. p. 210°, is also formed. The dihydrazide forms a *dihydrochloride*, needles, m. p. 174°, a *dibenzylidene* derivative, tablets, m. p. 218° (decomp.), and a *diisopropylidene* derivative, m. p. 174°. The action of sodium nitrite on a cold hydrochloric acid solution of the dihydrazide (dihydrochloride) gives *azidosuccinylglycineazide*,  $\text{N}_3\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$ , white, glistening leaflets, which is converted by warming with alcohol in ethereal solution into the corresponding *diurethane*, small, colourless, anisotropic prisms, m. p. 150—152° (decomp.). The hydrolysis of the latter by heating at 100° with alcoholic hydrogen chloride solution does not give ethyl  $\beta$ -aminopropionate, but a product which reacts with benzenesulphonyl chloride to give a compound, m. p. 125—127°; this result is not due to decomposition of the expected amino-ester, since this is unaffected by alcoholic hydrogen chloride at 100°. However, ethyl  $\beta$ -aminopropionate hydrochloride is produced by hydrolysing the urethane, using aqueous hydrochloric acid, although the yield never exceeds 30% of theory. It was expected that the hydrolysis of the above diazide, by means of boiling alcoholic hydrogen chloride, would give formaldehyde ammonia, carbon dioxide, and  $\beta$ -aminopropionic acid (cf. Curtius and Sieber, A., 1921, i, 653), but hydrazoic acid, succinic acid, and aminoacetic acid are formed

instead. The action of aniline on a freshly prepared, ethereal solution of the diazide gives a small quantity of a crystalline substance, m. p.  $195^{\circ}$ , perhaps the normal dianilide, together with the semi-inverted *dianilide*, colourless prisms, m. p.  $223-224^{\circ}$ ,  $N_3CO[(CH_2)_3CO\cdot NH\cdot CH_2\cdot CO\cdot N_3 + 2NH_2Ph =$



The constitution of this dianilide follows, since it gives aniline, aminoacetic acid, and phenyl- $\beta$ -carbamidopropionic acid,  $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot CO_2H$ , when hydrolysed by heating at  $100^{\circ}$  with concentrated hydrochloric acid. The cyclic *carbimide*,



(decomp.), is obtained by boiling a carbon tetrachloride solution of the diazide; it is very readily converted by the action of heat, even during its preparation, into an amorphous, infusible substance. The freshly prepared carbimide readily reacts with ethyl alcohol to give the analogous *urethane*, colourless prisms, m. p.  $124^{\circ}$ , and not the diurethane, m. p.  $150-152^{\circ}$  (decomp.) (above). It is evident that the cyclic carbimide is formed by isomeric change from the open-chain isomeride,  $CO\cdot N\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot N\cdot CO$ , which is not isolated. The cyclic carbimide reacts immediately in carbon tetrachloride solution with aniline or *p*-toluidine to give, respectively, the *anilide*, a colourless, microcrystalline powder, m. p.  $183^{\circ}$  (decomp.), or the *p*-toluidide, m. p.  $205^{\circ}$ . The hydrolysis of the cyclic urethane by means of hot ( $100^{\circ}$ ) concentrated hydrochloric acid gives  $\beta$ -aminopropionic acid, as expected, together with an infusible, colourless, somewhat insoluble compound, long, tabular crystals, which is converted into  $\beta$ -aminopropionic acid by further heating with acid at  $110^{\circ}$ ; moreover, this compound is not isolated if the original hydrolysis is conducted at this temperature.

Ethyl *N*-succinylamidoacetate is formed when succinyl chloride reacts with the hydrochloride of ethyl aminoacetate, but if the free ester is used, the product is ethyl succinyldiamidoacetate. This reacts with cold hydrazine hydrate to give the *dihydrazide*,  $C_2H_4(CO\cdot NH\cdot CH_2\cdot CO_2Et)_2$ , glistening tablets, m. p.  $220^{\circ}$ , which gives a *dibenzylidene* derivative. If the condensation with hydrazine hydrate is carried out in alcoholic solution, a flocculent *hydrazide*, m. p.  $225^{\circ}$ , is produced, which gives a compound, m. p.  $196^{\circ}$ , by reaction with benzaldehyde.

The dihydrochloride, m. p. above  $270^{\circ}$  (colourless tabular crystals), of ethylenediamine is produced by keeping a hydrochloric acid solution of the diazide of succinic acid, formed by diazotising the dihydrazide. When the diazide is boiled in chloroform solution, *ethylenedicarbimide*,  $C_2H_4(N\cdot CO)_2$ , b. p.  $75^{\circ}/25$  mm., or  $105^{\circ}/50$  mm., is produced, from which the known diurethane is formed by warming with anhydrous ethyl alcohol. The dicarbimide readily reacts with water, giving carbon dioxide and ethylenecarbimide, together with a small quantity of a compound (?  $C_3H_5O_2N_3$ ), small, thin, elongated, feld prisms, m. p. above  $300^{\circ}$ , which is also formed when the dicarbimide is kept in contact with moist air. The

dicarbimide reacts in carbon tetrachloride solution with aniline to give *ethylenediphenylcarbamide*,  $C_6H_5(NH\cdot CO\cdot NHPh)_2$ , prisms, m. p.  $245^\circ$  (decomp.). The action of aniline in ethereal solution on the diazide gives the dianilide of succinic acid. W. S. N.

**The Constitution of Carbamides. XV. A Delicate and Trustworthy Test for the Recognition of Cyanic Acid.** EML. ALPHONSE WERNER (T., 1923, 123, 2577—2579).

**Substituted Biurets and Allophanic Esters.** HEINRICH BILTZ and ARNOLD JELTSCH (Ber., 1923, 56, [B], 1914—1926).—Up to the present the systematic preparation of alkylated biurets has not been effected. It can be accomplished by the action of ammonia or amines on allophanic esters, which may be prepared from carbamides and chloroformic esters or from carbamic esters and carbamyl chloride. A second method depends on the action of alkylcarbimides on carbamides, reaction occurring initially at the primary amino-group. The new biurets closely resemble in their behaviour those described previously. The action of nitrous acid leads to the introduction of the nitroso-group at the terminal secondary nitrogen atom. Treatment with acetyl chloride causes the introduction of an acetyl group at a terminal nitrogen atom; it has not been established whether the change occurs at the primary or secondary amino-group.

It is proposed to distinguish the terminal nitrogen atoms by the expression  $N^*$ , whereas the intermediate atom is designated  $N^m$ .

Ethyl allophanate, m. p.  $190-191^\circ$ , and methyl allophanate, m. p.  $208^\circ$ , are prepared from carbamide and the requisite chloroformic ester according to the method of Dains and Wertheim (A., 1921, i, 61). Methyl  $N^*$ -methylallophanate, from methylcarbamide and methyl chloroformate at  $110-115^\circ$ , has m. p.  $163^\circ$ . Methyl  $N^m$ -methylallophanate, indistinct leaflets, m. p.  $146^\circ$ , is prepared from methyl methylcarbamate and carbamyl chloride; it is transformed by ammonia into *ms*-methylbiuret. Methyl- $N^m$ -ethylallophanate, m. p.  $160-161^\circ$ , is prepared in a similar manner to the corresponding methylallophanate; it is converted by aqueous or alcoholic solution of ammonia or ethylamine into ammonium  $N^m$ -ethylallophanate, m. p.  $226-228^\circ$ , and ethylammonium  $N^m$ -ethylallophanate, m. p.  $222-223^\circ$ , respectively. Phenylurethane and carbamyl chloride yield ethyl  $N^m$ -phenylallophanate, short, four-sided prisms or rhombic plates, m. p.  $184^\circ$ . Attempts to cause interaction between urethanes and dimethylcarbamyl chloride or between chloroformic esters and *s*- or *as*-dimethylcarbamide at  $100^\circ$  were unsuccessful.

$\omega$ -Methylbiuret is prepared from allophanic ester and aqueous methylamine (33%) at  $100^\circ$  from methyl  $N^*$ -methylallophanate and ammonia or from carbamide and methylcarbimide; it has m. p.  $167-168^\circ$ .  $\omega$ -Nitroso- $\omega$ -methylbiuret forms minute crystals, decomp.  $139-140^\circ$ ; it is decomposed by warm water in accordance with the equation:  $NH_2\cdot CO\cdot NH\cdot CO\cdot NMe\cdot NO + H_2O = CO(NH_2)_2 + CO_2 + N_2 + MeOH$ . Acetyl- $\omega$ -methylbiuret, from  $\omega$ -methylbiuret and acetyl chloride at  $100^\circ$ , has m. p.  $212^\circ$ .

*ω*-Ethylbiuret is readily prepared from aqueous ethylamine and methyl (but not ethyl) allophanate; it has m. p. 154° (cf. Pickard, Allen, Bowdler, and Carter, T., 1902, 81, 1572). *ω*-Nitroso-*ω*-ethylbiuret forms small, flat prisms, m. p. 119–120° (decomp.), whereas acetyl-*ω*-ethylbiuret crystallises in four-sided, oblique prisms, m. p. 160–162°.

The action of dimethylamine on methyl allophanate leads to the formation of *as*-dimethylcarbamide, m. p. 180°; dimethylcarbamyl chloride could not be caused to react with carbamide, methylcarbamide, or *s*-dimethylcarbamide.

*ωω'*-Dimethylbiuret, long, four-sided, flattened prisms, m. p. 162–163°, is prepared from methyl *N*<sup>ω</sup>-methylallophanate and methylamine or from methylcarbamide and methylcarbamide. *ω*-Nitroso-*ωω'*-dimethylbiuret, short, slender prisms, decomp. about 108°, *ωω'*-dinitroso-*ωω'*-dimethylbiuret, yellow, four-sided prisms, decomp. 94°, and *ω*-acetyl-*ωω'*-dimethylbiuret, minute crystals, m. p. 216–217° (decomp.), are described. Attempts to prepare *ωωω'*-trimethylbiuret from methyl *N*<sup>ω</sup>-methylallophanate and aqueous dimethylamine led to the production of *as*-dimethylcarbamide and methylcarbamide. Ethylcarbamide and ethylcarbimide at 100° yield a substance, C<sub>6</sub>H<sub>11</sub>ON<sub>3</sub>, leaflets, m. p. 191°, in place of the expected *ωω'*-diethylbiuret.

*ms*-Methylbiuret, colourless, four-sided prisms, m. p. 189°, is prepared from methyl *N*<sup>ms</sup>-methylallophanate and aqueous ammonia at 100°; it does not yield a nitroso-compound. *ω*-Acetyl-*ms*-methylbiuret forms indistinct crystals, m. p. 280°. Attempts to prepare *ω*-*ms*-dimethylbiuret from methyl *N*<sup>ms</sup>-methylallophanate and methylamine or from carbamyl chloride and *s*-dimethylcarbamide did not lead to the desired result; the action of cyanic acid on a solution of *s*-dimethylcarbamide in chloroform give a substance, C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>N<sub>3</sub>, m. p. 189–190°.

The preparation of *ms*-ethylbiuret is beset with difficulty owing to the ready hydrolysis of *N*<sup>ms</sup>-ethylallophanic esters by ammonia and amines, but, under certain conditions, it may be obtained from the methyl ester and aqueous ammonia; it crystallises in monoclinic or triclinic plates, m. p. 178–179°. *ω*-Acetyl-*ms*-ethylbiuret forms lustrous, hexagonal platelets, m. p. 228–230°. *ω*-*ms*-Diethylbiuret could not be prepared from methyl *N*<sup>ms</sup>-ethylallophanate and ethylamine since hydrolysis of the ester could not be avoided.

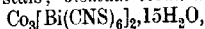
*ms*-Phenylbiuret, leaflets, m. p. 192°, is readily prepared from ethyl *N*<sup>ms</sup>-phenylallophanate and concentrated aqueous ammonia at 100°. *ω*-Methyl-*ω'*-phenylbiuret, coarse, four-sided prisms, m. p. 172–173°, is obtained from methylcarbamide and phenylcarbimide at 120–130°.

*s*-Dimethylcarbamide and methylcarbimide at 100° yield *ω*-*ms*-*ω'*-trimethylbiuret, long, slender, colourless needles, m. p. 125–126°. The microcrystalline *dinitroso*-derivative, decomp. 102°, and the *monoacetyl* compound, m. p. about 165°, are described. Corresponding attempts to prepare *ω*-*ms*-*ω'*-triethylbiuret were unsuccessful.

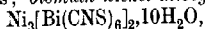
H. W.

**Some Complex Thiocyanates of Bismuth.** A. PACTELLO and N. FOÀ (*Gazzetta*, 1923, **53**, 526—531).—The addition of potassium thiocyanate solution to bismuth thiocyanate solution yields an orange-red coloration, which indicates the formation of the complex ion  $\text{Bi}(\text{CNS})_6'''$ . This indication is confirmed (1) by the existence of a series of salts capable of representation by a common scheme, this holding for the salt of cobalt, which exhibits a marked tendency to the formation of complex ions; (2) by the comparative stability of these salts towards the hydrolysing action of water, and (3) by the migration of complex bismuth-ions towards the positive pole in solutions of the salts. It seems probable that solutions of bismuth thiocyanate in thiocyanic acid contain bismuththiocyanic acids of the formula  $\text{HBi}(\text{CNS})_4$  in concentrated solutions or  $\text{H}_3\text{Bi}(\text{CNS})_6$  in dilute solutions; the structure of bismuth thiocyanate may be regarded as  $\text{BiBi}(\text{CNS})_8$ .

*Bismuth zinc thiocyanate*,  $\text{Zn}_3[\text{Bi}(\text{CNS})_6]_2$ , forms large, non-hygroscopic, orange-red crystals; *bismuth cobalt thiocyanate*,



reddish-brown crystals; *bismuth nickel thiocyanate*,



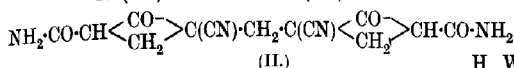
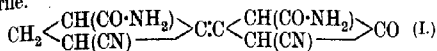
a greenish-yellow, crystalline mass becoming brownish-yellow when pounded; *bismuth vanadyl thiocyanate*,  $(\text{VO})_3[\text{Bi}(\text{CNS})_6]_2 \cdot 7\text{H}_2\text{O}$ , a reddish-violet powder; *bismuth iron thiocyanate*,  $\text{FeBi}(\text{CNS})_6$ , lustrous, green crystals; *bismuth thallium thiocyanate*,  $\text{TlBi}(\text{CNS})_6$ , red crystals, giving an orange-red powder. T. H. P.

**Methylenebismalononitrile and Hexacyanopentane and their Behaviour towards Hot Water.** OTTO DIELS and BRUNO CONN (*Ber.*, 1923, **56**, [B], 2076—2082).—A further investigation of the condensation of formaldehyde with malononitrile (cf. Diels, Gärtner, and Kaack, this vol., i, 25).

It has not yet been found possible to isolate the primary product of the action of formaldehyde on malononitrile in the presence of piperidine, but the production of methylenemalononitrile may be assumed from the formation of methylenebismalononitrile (m. p.  $160-180^\circ$  after softening very sharply at  $136-137^\circ$ , which is previously recorded as the melting point), and of *pentane-xx-yy- $\alpha$ -hexanitrite*, colourless leaflets, m. p.  $226^\circ$ , decomp.  $275^\circ$  after darkening at about  $180^\circ$ . The production of these substances is explained by the schemes:  $\text{CH}_2\text{C}(\text{CN})_2 + \text{CH}_2(\text{CN})_2 \rightarrow \text{CH}_2[\text{CH}(\text{CN})_2]_2$  and  $\text{CH}(\text{CN})_2 \cdot \text{OH}_2 \cdot \text{CH}(\text{CN})_2 + \text{CH}_2\text{C}(\text{CN})_2 \rightarrow (\text{CN})_2\text{C}[\text{CH}(\text{CN})_2]_2$ . Support of this hypothesis is found in the observation that the hexanitrite is obtained by the action of hot water on pure methylenebismalononitrile under definite conditions and by the spontaneous evaporation of alcoholic solutions of methylenebismalononitrile at the atmospheric temperature.

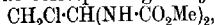
Methylenebismalononitrile is decomposed in a complicated manner by hot water, yielding the ammonium salts of two acids,  $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_4$ , small, pale yellow prisms, decomp.  $290^\circ$ , and  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_4$ , long, thin prisms, decomp.  $293^\circ$ , to which the constitutions (I) and (II) are assigned. The substance

$C_{12}H_{10}O_3N_4$  is also obtained by the action of hot water on pentane-hexanitride.



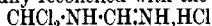
H. W.

**The Sandmeyer Synthesis of Ethyl Chloroimidocarbonate, and the Formhydroxamic Esters as a Step towards Alkyl Cyanates.** J. HOUBEN (*J. pr. Chem.*, 1922, [ii], 105, 7–26) [with E. PFANKUCH and K. KÜHLING.]—The preparation of ethyl *N*-chloroimidocarbonate is improved by working at twice the dilution employed by Sandmeyer (A., 1886, 611). In this reaction,  $\beta$ -chloroethylidenediurethane is also formed, evidently by the condensation of chloroacetaldehyde with 2 mols. of urethane; this compound is most conveniently prepared, in 93% yield, by gently warming a mixture of 2 mols. of urethane and 1 mol. of  $\alpha,\beta$ -dichloro-ether. The corresponding *methyl* ester,

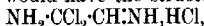


forms colourless crystals, m. p. 136°. The action of chlorine on an ice-cold, aqueous solution of urethane gives *N*-dichlorourethane,  $\text{NCl}_2\cdot\text{CO}_2\text{Et}$ , a golden-yellow oil, b. p. 66–67°/18 mm., which has an extraordinarily penetrating and stupefying odour. It is volatile in steam, and dissolves in warm ammonium chloride solution. It decomposes potassium nitrite solution, giving a green coloration, and liberates iodine from potassium iodide solution. On being heated above its boiling point (147°/ordinary pressure), it decomposes with violence. When kept in alcoholic solution it passes into  $\beta$ -chloroethylidenediurethane. The analogous *methyl* ester,  $\text{NCl}_2\cdot\text{CO}_2\text{Me}$ , prepared similarly, is a yellow oil, b. p. 56–57°/21 mm., having properties similar to those of its homologue. Ethyl imidocarbonate reacts in alcoholic solution with aniline hydrochloride to give a small quantity of *s*-diphenylcarbamide, together with *ethyl phenylimidocarbonate*,  $\text{NPh}\cdot\text{C}(\text{OEt})_2$ , a somewhat oily, but mobile liquid, b. p. 136–137°/16 mm., which is readily decomposed by means of dilute mineral acids into aniline and ethyl carbonate. The oxime of ethyl formate, *ethyl formhydroximate*,  $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{OEt}$ , long, colourless needles, m. p. 80°, b. p. 76–77°/15 mm. (slight decomp.), is prepared by the action of free hydroxylamine on free ethyl imidoformate (both liberated from their hydrochlorides by means of potassium hydroxide) in ice-cold, aqueous solution, or by the action of hydroxylamine on ethyl imidoformate hydrochloride in dry ethereal solution. It readily reacts with acetic anhydride, giving the *acetate*,  $\text{OEt}\cdot\text{CH}\cdot\text{NOAc}$ , an oil, b. p. 82°/17 mm. *Methyl formhydroximate*, needles, m. p. 99–100°, and *n*-propyl *formhydroximate*, long needles, m. p. 61–62°, can only be prepared in anhydrous ethereal solution, using free hydroxylamine. These three oximino-esters give a transient, bluish-green coloration with chlorine in carbon tetrachloride solution, and a slight reddish-brown or reddish-yellow coloration

with aqueous ferric chloride solution. *Formylformamidozine*,  $\text{CHO}\cdot\text{NH}\cdot\text{CH}\cdot\text{NOH}$ , m. p.  $140^\circ$  (slight decomp.), is prepared by the action of hydrogen cyanide sesquihydrochloride,  $2\text{HCN}\cdot 3\text{HCl}$  (Claisen and Matthews, *Ber.*, 1883, **16**, 311) (1 mol.), on an ice-cold, aqueous-ethereal solution containing 1 mol. of free hydroxylamine and 2 mols. of potassium hydroxide. The production of this compound is readily reconciled with the formula

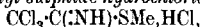


(Gattermann, A., 1898, i, 546), for the sesquihydrochloride, whereas if the latter is derived from Nef's imidoformyl cyanide (A., 1896, i, 71),  $\text{NH}\cdot\text{CH}\cdot\text{CN}$ , it would have the structure



and would give, by the action of hydroxylamine, the isomeric, known oximidoacetamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{NOH}$ . It seems likely, therefore, that Nef's dimeric hydrogen cyanide has the structure  $\text{NH}\cdot\text{CH}\cdot\text{NC}$ .  
W. S. N.

**Trichloroacetimidomethyl Sulphide.** WILHELM STEINKOPF and SIEGFRIED MÜLLER (*Ber.*, 1923, **56**, [B], 1930—1932).—*Trichloroacetimido methyl sulphide hydrochloride*,



large, rhombic crystals, m. p.  $126\text{--}129^\circ$ , according to the manner of heating, is prepared by the action of dry hydrogen chloride on a solution of trichloroacetonitrile in methyl mercaptan. It is converted by cold water into a mixture of the *S*-methyl ester of trichlorothioacetic acid,  $\text{CCl}_3\cdot\text{CO}\cdot\text{SMe}$ , and *trichloroacetimido methyl sulphide*. The latter substance, a pale yellow liquid, b. p.  $93\text{--}5^\circ/20$  mm., which slowly decomposes when preserved at the atmospheric temperature, is obtained in the homogeneous condition by the addition of the hydrochloride to a saturated, ice-cold solution of potassium carbonate in water in the presence of ether. H. W.

**Diallylhydrazine and its Conversion into Tetra-allyltetrazen by Dehydrogenation with Azodicarboxylic Ester.** OTTO DIELS (*Ber.*, 1923, **56**, [B], 1933—1938).—Ethyl azodicarboxylate appears to be a generally applicable reagent for the conversion of disubstituted hydrazins into tetrazens. A tetrazen appears to be produced initially which subsequently passes into the tetrazen and the hydrazo-ester:  $2\text{NR}_2\cdot\text{NH}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et} \rightarrow 2\text{NH}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et} + \text{NR}_2\cdot\text{N}\cdot\text{N}\cdot\text{NR}_2$  (cf. Busch, Müller and Schwarz, this vol., i, 864).

Methyl hydrazinemonocarboxylate is converted by allyl bromide into *methyl diallylhydrazinemonocarboxylate*,  $\text{N}(\text{C}_3\text{H}_5)_2\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , colourless, lustrous needles, m. p.  $68^\circ$ ; the corresponding *hydrochloride* is very hygroscopic. The ester combines with bromine in the presence of chloroform to give *methyl tetrabromodipropylhydrazinemonocarboxylate*, colourless crystals, m. p.  $108^\circ$ . Allyl bromide and ethyl hydrazinemonocarboxylate give a mixture of *ethyl diallylhydrazinemonocarboxylate*, short, lustrous needles, m. p.  $52^\circ$ , and *ethyl monoallylhydrazinemonocarboxylate*, a colourless liquid, b. p.  $102^\circ/18$  mm. Methyl diallylhydrazinemonocarboxylate is converted by hydrazine hydrate at  $150^\circ$  into *as-diallylhydrazine*,

colourless, mobile liquid, b. p.  $145^{\circ}/752$  mm., which is transformed by furfuraldehyde into *furfuraldehydediallylhydrazone*, a colourless liquid, b. p.  $108^{\circ}/2$  mm., and by phenylcarbimide into *phenyldiallylsemicarbazide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{C}_3\text{H}_5)_2$ , a colourless, viscous liquid, b. p.  $185^{\circ}/0.5$  mm. Diallylhydrazine is converted by ethyl azodicarboxylate in well-cooled, ethereal solution into *tetra-allyltetrazen*,  $\text{N}(\text{C}_3\text{H}_5)_2\cdot\text{N}\cdot\text{N}\cdot\text{N}(\text{C}_3\text{H}_5)_2$ , a pale yellow, mobile liquid, b. p.  $113^{\circ}/152$  mm., which explodes violently when heated above its boiling point; the corresponding picrate and the additive compound with mercuric chloride do not crystallise readily.

Diphenylhydrazine and azodicarboxylic ester give tetraphenyltetrazen and the hydrazo-ester.

Phenylmethylhydrazine is converted by ethyl azodicarboxylate into diphenyldimethyltetrazen, m. p.  $137^{\circ}$ ; simultaneously phenylazide, b. p.  $70^{\circ}/11$  mm., and phenylmethylethane, b. p.  $116^{\circ}/1$  mm., are produced.

H. W.

**Certain Simple Aliphatic Azo-compounds.** F. ARNDT, J. MILDE, and G. ECKERT (*Ber.*, 1923, 56, [B], 1976—1984).—*Dimethylazodicarbothioamide*,  $\text{NH}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{SMe})\cdot\text{NH}$ , is prepared by the oxidation of the corresponding hydrazo-compound by potassium ferrieyanide in alkaline solution; it crystallises in orange-red needles, m. p.  $92$ — $93^{\circ}$ , which can be preserved at  $0^{\circ}$  during one to two days, but decompose within a few hours at the atmospheric temperature. It decomposes violently when heated at about  $110^{\circ}$  into the hydrazo-compound, nitrogen, cyanogen, dimethyl disulphide, and methyl thiocyanate, in accordance with the equations:  $2\text{C}_4\text{H}_9\text{N}_4\text{S}_2 = \text{C}_4\text{H}_{10}\text{N}_4\text{S}_2 + \text{N}_2 + \text{C}_2\text{N}_2 + \text{SMe}\cdot\text{SMe}$  and  $\text{C}_4\text{H}_9\text{N}_4\text{S}_2 = \text{C}_4\text{H}_{10}\text{N}_4\text{S}_2 + \text{N}_2 + 2\text{Me}\cdot\text{SCN}$ . It is immediately dissolved by dilute mineral acids with the formation of colourless solutions which do not evolve gas and contain mainly the hydrazo-compound. The course of the action has been more fully investigated by using the *azo-hydrochloride*,  $\text{C}_4\text{H}_{10}\text{N}_4\text{S}_2\text{Cl}_2$ , a reddish-brown substance which rapidly becomes white when exposed to moisture. It is thereby decomposed into the hydrazo-hydrochloride, urazole, methylsulphonyl chloride, ammonium chloride, and the *hydrochloride* of the *methylsulphone of dithiourazole dimethyl ether* in accordance with the scheme:  $6\text{C}_4\text{H}_9\text{N}_4\text{S}_2\cdot 2\text{HCl} + 6\text{H}_2\text{O} = 4\text{C}_4\text{H}_{10}\text{N}_4\text{S}_2\cdot 2\text{HCl} + 3\text{H}_2\text{O}_2\text{N}_2\text{S}_3\cdot\text{HCl} + \text{C}_2\text{H}_5\text{O}_2\text{N}_2 + \text{Me}\cdot\text{SO}_2\text{Cl} + 2\text{NH}_4\text{Cl}$ . The *methylsulphone of dithiourazole dimethyl ether*,  $\frac{\text{N}\cdot\text{C}(\text{SMe})}{\text{N}\cdot\text{C}(\text{SMe})} > \text{N}\cdot\text{SO}_2\text{Me}$ , m. p.  $102^{\circ}$ ,

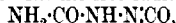
readily prepared from dithiourazoledimethyl ether and methylsulphonyl chloride in ammoniacal solution.

*Methyl hydrazodithiocarboxylate*,  $\text{SMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{SMe}$ , needles, m. p.  $173^{\circ}$ , prepared from hydrazine and methyl chlorothioformate, oxidised by nitric acid (60—66%) to the corresponding *azo-ester*,  $\text{H}_6\text{O}_2\text{N}_2\text{S}_2$ , lustrous, orange-red needles, m. p.  $69^{\circ}$ , which is stable at the atmospheric temperature. It is decomposed by heat in accordance with the schemes:  $\text{SMe}\cdot\text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{SMe} \rightarrow \text{MeS}\cdot\text{SMe} + \text{N}_2 + 2\text{CO}$  or  $\rightarrow \text{MeS}\cdot\text{CO}\cdot\text{CO}\cdot\text{SMe} + \text{N}_2$ . (*Methyl dithioazolate*, a yellow, crystalline powder, m. p.  $80^{\circ}$ , b. p.  $218^{\circ}/760$  mm.,

is also prepared from oxalyl chloride and methyl mercaptan in the presence of anhydrous ether.) Dilute sodium hydroxide solution decomposes it instantaneously, giving the hydrazo-ester, dimethyl disulphide, nitrogen, and carbon dioxide.

*Methyl chlorothioformate*,  $\text{COCl}\cdot\text{SMe}$ , a colourless, mobile, highly refractive liquid, b. p.  $110^\circ$ , is prepared by the interaction of well-cooled carbonyl chloride and methyl mercaptan in the presence of a trace of aluminium chloride. *Methyl chlorodithioformate*,  $\text{CSCl}\cdot\text{SMe}$ , a golden-yellow liquid, b. p.  $50\text{--}52^\circ/15\text{ mm.}$ , is prepared in a similar manner from thiocarbonyl chloride and methyl mercaptan. H. W.

**The Decomposition of Carbamyl Azide,  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3$ , alone and in Aromatic Hydrocarbons.** THEODOR CURTIUS and FRIEDRICH SCHMIDT (*J. pr. Chem.*, 1923, [ii], **105**, 177—198).—Carbamyl azide decomposes when heated alone, with the formation of isocyanic acid and hydrazoic acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3=\text{NH}\cdot\text{CO}+\text{N}_2\text{H}$ ; the latter gives nitrogen and ammonium azide. Decomposition also occurs in the sense of the equation:  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3=\text{N}_2+\text{NH}_2\cdot\text{CO}\cdot\text{N}<$ , giving a free radicle, two molecules of which may then combine to form azodicarbonamide. The latter is converted by boiling with water, whilst working up the product, into hydrazodicarbonamide. Urazole is also produced, perhaps by the interaction of isocyanic acid with the free radicle to give



which spontaneously passes into urazole,  $\text{NH}<\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ . But perhaps

decomposition is accompanied by rearrangement:  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3=\text{N}_2+\text{NH}_2\cdot\text{N}\cdot\text{CO}$ ; this rearranged residue could also combine with isocyanic acid to give  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CO}$ , which would then isomerise to urazole. The relative merits of these explanations remains undecided, although the formation (momentarily) of a free radicle seems probable, because a diarylcarbamide is also produced if the heating is conducted in a solution in an aromatic hydrocarbon, the first product being presumably a monoaryl carbamide, which then suffers rearrangement:  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3+\text{C}_6\text{H}_5=\text{N}_2+\text{NH}_2\cdot\text{CO}\cdot\text{NHPh}$ . Carbamyl azide reacts with boiling ethyl alcohol to give urethane and hydrazoic acid. The complex carbamide,  $(\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH})_2$  (Pellizari, A., 1907, i, 833), gives amino-urazole,  $\text{NH}_2\cdot\text{N}<\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , when heated at  $150^\circ$  with water.

W. S. N.

**Low Temperature Tar. III.** FRANZ SCHÜTZ, WILHELM BUSCHMANN, and HEINRICH WISSEBACH (*Ber.*, 1923, **56**, [B], 1967—1975; cf. this vol., i, 195, 525).—The phenols and bases present in the low temperature tar obtained from the Fürst Hardenburg coal in rotary furnaces at a temperature not exceeding  $500^\circ$  are described.

The phenols are isolated in the usual manner from the low temperature tars and are subjected to preliminary purification by fractional distillation, thus yielding almost colourless fractions.

which alter little on exposure to air. The viscosity increases rapidly with increasing temperature, but the separation of a solid is not observed in any case. They contain small amounts of substances containing sulphur and nitrogen, together with very unstable products of unknown nature, which, however, are readily removed by hot water. Mercaptans are removed by precipitation with lead acetate in alcoholic solution. The separation of the individual phenols by fractional distillation is exceedingly tedious and only completely successful in the case of phenol, whereas the higher homologues are almost inextricably mixed. Their isolation can only be accomplished by the application of physical and chemical methods, which vary from case to case (they are described fully in the original). The presence of the following eight phenols has been established: phenol, *o*-, *m*-, and *p*-cresols, and 1:3:5-, 1:2:4-, 1:3:4-, and 1:4:2-xyleneols. The fractions of higher boiling point have not been completely investigated; they do not appear to contain naphthols.

The bases investigated are derived exclusively from the crude light oils of the tar in which they are present to the extent of about 1%. On distillation, the mixture gives the fractions, b. p. 93—150° (18%), 150—200° (27%), and 200—250° (55%). Resinifiable or pitch-like substances or compounds which are readily polymerised by acids or alkalis are not present. Pyridine is easily isolated from the fractions of lower boiling point. The separation of individuals from the fractions of higher boiling point is very incomplete. The identification of the components is therefore effected by methods which are suited to each particular case. The presence of pyridine, 2-methylpyridine, 2:3-dimethylpyridine, 2:4-dimethylpyridine, 2:4:6-trimethylpyridine, aniline, quinoline, and 2-methylquinoline is established.

H. W.

**Certain Derivatives of 1-Methyl- $\Delta^1$ -cyclohexene.** S. NAMETKIN and ANNA JARZEV (*Ber.*, 1923, 56, [B], 1803—1804).—The authors have undertaken an examination of the influence of the particular agent used in the oxidation of unsaturated hydrocarbons on the configuration of the glycol so produced; the oxidation of 1-methyl- $\Delta^1$ -cyclohexene is described.

1-Methyl- $\Delta^1$ -cyclohexene, b. p. 109—110°/753 mm.,  $d_4^{20}$  0.8122,  $n_D^{20}$  1.4503, is conveniently prepared by the action of dilute nitric acid ( $d$  1.075) at 100—110° or of sulphuric acid (50%) on 1-methylcyclohexan-1-ol. It is oxidised by benzoyl peroxide in ethereal solution (cf. Prileschaev, A., 1910, i, 86, 295; 1911, i, 255, 604; 1912, i, 633) to 1-methylcyclohexene 1-oxide,  $C_7H_{12}O$ , b. p. 137.5—138°/756 mm.,  $d_4^{20}$  0.9300,  $n_D^{20}$  1.4430, which is converted by water at 107—110° into *cis*-1-methylcyclohexane-1:2-diol, small, four-sided prisms, m. p. 84° (cf. Brunel, A., 1905, i, 869); the latter compound does not appear to become isomerised by treatment with water at 180°. *trans*-1-Methylcyclohexane-1:2-diol, m. p. 67°, is obtained by the oxidation of 1-methyl- $\Delta^1$ -cyclohexene with permanganate.

H. W.

**4-Methyl- $\Delta^1$ -cyclohexene and certain of its Derivatives.** S. NAMETKIN and LYDIA BRÜSSOV (*Ber.*, 1923, **56**, [B], 1807—1810).—4-Methyl- $\Delta^1$ -cyclohexene has been frequently described previously in the literature, but the products do not appear to have been homogeneous; the pure substance, b. p. 102.5—102.7°/772 mm.,  $d_4^{20}$  0.8001,  $n_D^{20}$  1.4419, is prepared by the successive treatment of 4-methylcyclohexane-1-ol with sodium, carbon disulphide, and ethyl sulphate, followed by thermal decomposition of the *xanthate* thus produced. Oxidation of the hydrocarbon by benzoyl peroxide in ethereal solution leads to the formation of 4-methylcyclohexene 1-oxide,  $C_7H_{12}O$ , b. p. 147—147.5°/16 mm.,  $d_4^{20}$  0.9364,  $n_D^{20}$  1.4473, which is transformed by water at 108—110° into *cis*-1-methylcyclohexane-4 : 5-diol, small rhombic crystals, m. p. 63—64°. *trans*-1-Methylcyclohexane-4 : 5-diol, long needles, m. p. 35—37°, is obtained by treatment of 4-methyl- $\Delta^1$ -cyclohexene with cold permanganate solution (1%). The physical constants of the diols indicate that in each case a mixture of the two theoretically possible *cis*- and *trans*-forms is produced.

H. W.

**Constitution of Benzene.** RONALD FRASER (*T.*, 1923, **123**, 2712—2713).

**Space Formulæ of Benzene, Naphthalene, and Anthracene.** B. ÜRELKIN (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 493—532).—The existing formulæ for aromatic compounds are criticised on the ground that none of them explains the peculiar "aromatic" character of the compounds or the reason why true aromatic character is not shown by cyclic compounds with five- or eight-membered rings, and an attempt is made to devise a formula satisfying the latter requirements.

In the first place, it is suggested that when an atom containing several electrons unites with a hydrogen atom with the formation of a ring or "octet" of eight electrons, the positive nucleus of the hydrogen atom may or may not enter the electronic sphere. In cases where the nucleus remains outside the sphere, the new compound will readily ionise and exchange the hydrogen atom for another atom, as in the example of hydrogen chloride; if the positive nucleus is within the electronic sphere the mobility of the hydrogen atom is diminished and the compound is less reactive or indifferent (*i.e.*, not ionised), as in ammonia or methane. From this argument it follows that a methyl group should be very similar to an atom of a halogen, and it is shown from crystallographic data that this assumption is justified; thus *p*-xylene is practically isomorphous with the *p*-dihalogenobenzenes. A double bond is described as an arrangement of four electrons disposed at the corners of a square so that the centres of the two atoms can be joined by a line perpendicular to the plane of this square and passing through its centre; the instability of the double bond is due to the displacement of the electrons necessitated by this arrangement. In a triple bond there are six electrons similarly

arranged at the corners of a hexagon; it is clear that free rotation is impossible with these two systems.

As regards the benzene formula itself, it is suggested that of the thirty electrons in benzene, twelve are used for the union of hydrogen with carbon; another twelve suffice to hold together the ring of six carbon atoms, whilst six electrons remain "free" and must assume some symmetrical arrangement within the molecule; this means that they must be disposed at the corners of a regular octahedron and one of the axes of this octahedron must coincide with the axis of symmetry of the molecule. This is achieved by disposing the nuclei of the carbon atoms in two parallel planes at the corners of equilateral triangles the sides of which are not parallel but form an angle of  $60^\circ$ ; in other words, in projection their apices form a regular hexagon. The six electrons occupy positions in the centres of the sides of these triangles. It is shown that taking the distance between two such electrons as 1, the distances between the centres of the nuclei of two meta-carbon atoms is equal to 2; that between the ortho-atoms is represented by  $\sqrt{2}$ , and between the para-atoms by  $\sqrt{6}$ ; or taking the ortho-distance as unit, we have  $o : m : p = 1 : \sqrt{2} : \sqrt{3}$ , that is, the same as in Sachse's formula. The electrons uniting the six-membered carbon ring are so disposed that the two electrons forming the ortho-bonds occupy two of the corners of a square, the other two corners being also occupied by electrons. This disposition simulates a double linking, but does not constitute one, because two of the four electrons are also involved in another similar arrangement. It is to this that the peculiar character of the aromatic nucleus is ascribed, and mathematical proof is given that such an arrangement is impossible with any number of carbon atoms other than six. The position of the electrons which unite the hydrogen atoms to the nucleus is somewhat difficult to describe without reference to drawings. A formula for naphthalene is constructed by fusing two benzene formulæ in the ortho-position, and a repetition of the process leads to that of anthracene and chrysene.

From these formulæ the crystal structure of benzene, naphthalene, and anthracene is deduced and is shown to agree satisfactorily with experimental data. The chief objection to the formulæ is the fact that benzene should exist in two enantiomorphous modifications, but it is suggested that the lack of symmetry in the new formula may be insufficient to cause rotation of polarised light.

G. A. R. K.

#### Diamond- and Graphite-structure in Organic Compounds.

A. SCHLEICHER (*J. pr. Chem.*, 1922, [ii], 105, 350—354).—The author traces a connexion between the structure of diamond and of graphite, and the phenomena connected with the ethylation of benzene, and the phenylation of ethane.

W. S. N.

Additive Compounds of Aluminium Chloride with Hydrocarbons. A. SCHLEICHER [with E. BÜTTGENBACH] (*J. pr. Chem.*, 1922, [ii], 105, 355—360).—By the action of aluminium chloride

on a mixture of benzene and ethyl bromide, a yellow oil is obtained one fraction of which has b. p. 135—138°/12 mm. (slight decomp.). The oily product formed by heating aluminium chloride with hexaethylbenzene at a temperature not exceeding 90° is less easily attacked by water than aluminium chloride itself. These results, it is claimed, prove the existence of additive compounds of aluminium chloride with triethylbenzene and hexaethylbenzene, confirming the conclusions of Gustavson (A., 1905, i, 696). W. S. N.

**The Refractometric Behaviour of Cymene from Sulphite-Cellulose Liquors.** A. KARVONEN (*Ber.*, 1923, 56, [B], 1824—1828).—The author notes the many discrepancies between the published values for the refractive index and the density of cymene from various sources. He therefore submits *p*-cymene from the sulphite liquors of the Finnish cellulose industry to severe chemical and physical treatment, finally washing with strong sulphuric acid and distilling over sodium. In this way, nine samples are obtained, b. p. 174·8°/746·5 mm., with  $n_D^{20}$  between 1·49032 and 1·49089, mean 1·49060, and  $d_4^{20}$  0·85668—0·85704, mean 0·85688. H. H.

**The Aryl and Alkyl Sulphonamides.** PERCIVAL WALTER CLUTTERBUCK and JULIUS BEREND COHEN (*T.*, 1923, 123, 2507—2515).

**Hydrogenated Polycyclic Ring Systems. II. The Stereoisomerism of Dicyclohexane.** WALTHER SCHRAUTH and KURT GÖRIG (*Ber.*, 1923, 56, [B], 1900—1906).—In a recent theoretical paper, Mohr (A., 1919, ii, 229) has considered the stability of the cyclohexane ring and has shown that the number of known isomerides is readily explicable by means of Sachse's model (in which the carbon atoms do not lie in one plane) if, at the same time, a free or only partly hindered rotation is assumed. For the establishment of the theory it is necessary that cyclohexane itself or one of its monosubstituted products should be isolated in at least two isomeric forms. The problem appears to be beset with unexplained difficulties in so far as simple derivatives are concerned. The authors have therefore directed their attention to compounds containing a second ring, and bring forward evidence of the existence of at least three dicyclohexanes.

The action of phosphoric oxide on a mixture of cyclohexanol and phenol leads to the production of a mixture of *p*-cyclohexylphenol, slender needles, m. p. 130°, b. p. 165°/15 mm., and *o*-cyclohexylphenol, needles, m. p. 57°, b. p. 147°/17 mm. Hydrogenation of the former compound in the presence of a nickel catalyst at 180—220° yields a mixture of *cis*-*p*-cyclohexylcyclohexanol, needles, m. p. 105°, b. p. 159°/20 mm., and *trans*-*p*-cyclohexylcyclohexanol, m. p. 83—84°, b. p. 157—158°/20 mm. *o*-cyclohexylcyclohexanol has b. p. 273—274·5°/750 mm.,  $d_4^{20}$  0·9835, and appears to possess a spatial configuration of the carbon skeleton differing from that of the compound described in the literature.

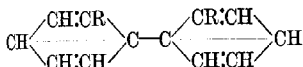
The action of zinc chloride on the two forms of *p*-cyclohexyl-

cyclohexanol yields cyclohexyl- $\Delta^1$ -cyclohexene, b. p. 236—237.5°/755 mm., which is hydrogenated to dicyclohexane, b. p. 227—228°/750 mm., the compound being identical with that described by Wallach. On the other hand, *o*-cyclohexylcyclohexanol does not yield a homogeneous hexene, the physical properties of the product appearing to be subject to uncontrollable factors. Hydrogenation of the material gives two different dicyclohexanes which have b. p. 219.5—221.5°/750 mm.,  $d_4^{20}$  0.8809,  $n_D^{20}$  1.47758, and b. p. 235—237°/750 mm.,  $d_4^{20}$  0.8818,  $n_D^{20}$  1.47795, respectively. The variety b. p. 235—237°/750 mm. appears to be the stable form, since it is unchanged by light or by energetic transforming agents. The remaining isomerides are transformed by warming with aluminium chloride or by protracted exposure to light into a mixture of the three forms, in which that of boiling point 235—237°/750 mm. predominates.

Evidence is brought forward to show that the hexene derivative mentioned previously can also exist in a labile form, b. p. 231.5—232.5°.

H. W.

**Stereoisomerism among Derivatives of Diphenyl.** E. E. TURNER (*Nature*, 1923, **112**, 439).—The possibility of the existence of a stable para-bond in benzene and diphenyl derivatives suggests that any 2 : 2'-derivative of diphenyl should be capable of optical activity on the basis of the annexed formula (cf. Kenner and others, T., 1922, **121**, 614, etc.). Four asymmetric carbon atoms exist also in the isomeric dinitrobenzidines and some of their derivatives (Brady and McHugh, T., 1923, **123**, 2047), although none are known to exhibit optical activity.



A. A. E.

**Stereoisomerism among Derivatives of Diphenyl.** J. KENNER (*Nature*, 1923, **112**, 539—540).—Although the formula considered by Turner (preceding abstract) contains four asymmetric carbon atoms, it does not demand the existence of a correspondingly large number of stereoisomeric forms of 2 : 2'-derivatives of diphenyl. The respective distributions of the groups attached to the pair of asymmetric carbon atoms in either benzene nucleus are not mutually independent, so that only one asymmetric atom in each nucleus is effective as a source of stereoisomerism.

A. A. E.

**The [Crystal] Lattice of Triphenylmethane.** H. MARK and K. WEISSENBERG (*Z. Physik*, 1923, **17**, 347—350).—Contrary to the conclusion of Becker and Rose (this vol., i, 550), the authors find, by Röntgen-ray analysis, that 8 molecules, and not 3, are contained in the elementary crystal cell of the stable crystalline modification of triphenylmethane. The respective lengths of the sides of the cell are :  $a$ , 15.16 Å.;  $b$ , 26.25 Å.;  $c$ , 7.66 Å., in agreement with values of the axial ratios deduced from goniometric

crystallographic measurements and with the results of Huggins (this vol., i, 329).

J. S. G. T.

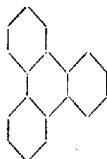
**The [Crystal] Lattice of Triphenylmethane.** KARL BECKER and H. ROSE (*Z. Physik*, 1923, 17, 351—352).—The authors reply to criticism of their results by Mark and Weissenberg (preceding abstract), and remark that possibly the crystals of triphenylmethane investigated by themselves possessed hexagonal symmetry. The question as to whether the different conclusions originate in the existence of different crystalline modifications of triphenylmethane is to be settled by a mutual interchange and reinvestigation of the crystals employed.

J. S. G. T.

**Hydrogenated Polycyclic Ring Systems. III. Perhydro-9:10-benzophenanthrene.** WALTHER SCHRAUTH and KURT GÖRIG (*Ber.*, 1923, 56, [B], 2024—2027).—The author has previously expressed the opinion that the carbohydrates of plants during their life, and more particularly during the formation of coal, give a primary condensation product which contains the carbon skeleton of 9:10-benzophenanthrene. The preparation of perhydro-9:10-benzophenanthrene has therefore been effected; it is possibly identical with the compound prepared by Willstätter and Kalb (*A.*, 1922, i, 989) by the reduction of lignin, cellulose, or sugar with phosphorus and hydriodic acid.

The action of phosphoric oxide on a mixture of *o*-cyclohexylcyclohexanol and phenol leads to the formation of 1-*o*-dicyclohexyl-2-phenol, needles, b. p. 220—224°/14 mm., m. p. 112—115°, together with a residue, m. p. 86—87°, which greatly resembles colophony. The phenyl is reduced by hydrogen in hexahydro-toluene solution in the presence of a nickel catalyst to 1-*o*-dicyclohexylcyclohexane-2-one, a colourless, very viscous liquid, b. p.

212—214°/14 mm.,  $d_4^{20}$  0.9874, which solidifies when cooled to a glassy, non-crystalline mass. Treatment of the ketone with zinc chloride at 180° yields  $\Delta^9$ -hexadecahydro-9:10-benzophenanthrene, a colourless liquid, b. p. 186—188.5°/12 mm.,  $d_4^{20}$  0.9518, which is hydrogenated in the presence of a nickel catalyst to perhydro-9:10-benzophenanthrene (annexed formula), a colourless liquid, b. p. 175—176°/7 mm.,  $d_4^{20}$  0.9425,



$n_D^{20}$  1.51959.

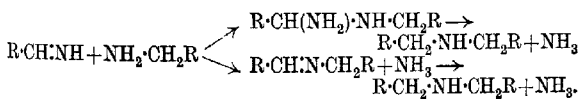
H. W.

**The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. II.** WILLIAM MURDOCH CUMMING (*T.*, 1923, 123, 2457—2464).

**The Utilisation of Monomethylaniline in the Production of Tetryl [2:4:6-Trinitrophenylmethylnitroamine].** THOMAS JOSEPH NOLAN and HENRY W. CLAPHAM (*Sci. Proc. Roy. Dubl. Soc.*, 1923, 17, 219—223).—Nitration of methylaniline with nitric acid in presence of sulphuric acid gives rise to a considerable amount of 2:3:4:6-tetranitrophenylmethylnitroamine (*m*-nitrotetryl) in addition to tetryl, and since, by hydrolysis, this gives *m*-hydroxy-

tetryl, which reduces the stability of tetryl, the method is not suitable for the manufacture of tetryl. On the other hand, phenylmethylnitrosoamine can be nitrated to give tetryl without the formation of any appreciable quantity of *m*-nitrotetryl. It is necessary to isolate the phenylmethylnitrosoamine and to nitrate it in freshly prepared sulphuric acid solution. There appears to be an equilibrium between nitrous acid, methylaniline, and phenylmethylnitrosoamine in sulphuric acid solution. Consequently, if the nitrosoamine is prepared in sulphuric acid solution, or if the nitrosoamine is dissolved in sulphuric acid and time allowed for equilibrium to be attained, methylaniline will be present and a good quality tetryl cannot be obtained on nitration. E. H. R.

**Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. VI. Nitriles.** JULIUS VON BRAUN, GEORG BLESSING, and FRIEDRICH ZOBEL (*Ber.*, 1923, **56**, [B], 1988—2001).—The catalytic hydrogenation of nitriles in the presence of nickel salts occurs rapidly and smoothly except in the cases of the simpler aliphatic nitriles, in the presence of which the catalyst rapidly becomes poisoned. It leads to the production of mixtures of primary and secondary, but apparently not of tertiary amines, the yields being 80–95% of those theoretically possible. Alteration in pressure does not appear to affect the course of the reaction; the influence of temperature is not very marked and is variable. On the other hand, the effect of solvent and of concentration is unusually marked. The total amount of reduced product is always somewhat greater in the presence of alcohols or ethers than in that of hydrocarbons, and a very marked displacement of the yield in the direction either of primary or secondary amine can be effected by variation of the oxygenated solvent. Increase in concentration in the cases of all solvents favours the production of primary base frequently to a very marked degree. The primary product of the change is assumed to be the compound  $R\cdot CH\cdot NH_2$ , which is either reduced further to primary amine or reacts with primary amine to produce the secondary base in accordance with the schemes:



The comparatively greater yield of primary amines in more concentrated solution is thereby explained. Confirmation of the hypothesis is found in the observation that under similar conditions the yields of secondary bases from ortho-substituted benzonitriles are less than from the corresponding meta- and para-derivatives, thus conforming to the expected influence of steric hindrance. Further, if alcohols with a particularly mobile hydroxyl group  $R'\cdot OH$  are used as solvents during the reduction of a nitrile,  $R\cdot CN$ , in addition to the bases  $R\cdot CH_2\cdot NH_2$  and  $NH_2(CH_2R)_2$ , mixed bases of the type  $R\cdot CH_2\cdot NHR'$  are produced, the formation

of which is explained by the scheme:  $R\cdot CH\cdot NH + R'\cdot OH \rightarrow R\cdot CH(OH)\cdot NHR' \rightarrow R\cdot CH\cdot NR' \rightarrow R\cdot CH_2\cdot NHR$ .

Hydrogenation is usually effected at 110–130°, and is continued until further appreciable absorption of the gas does not occur. The products are readily separated from one another by fractional distillation in all cases in which the solvent does not enter into the reaction; where this is the case, the separation of the two secondary bases is difficult.

Acetonitrile and propionitrile are only hydrogenated to a slight extent under the experimental conditions.

Oxonitrile gives *n*-octylamine, b. p. 72–73°/14 mm. (*hydrochloride*, m. p. 198°; *phenylthiocarbamide* derivative, m. p. 55°), and *dioctylamine*, b. p. 175°/14 mm. (*hydrochloride*, m. p. 238°).

$\gamma$ -Phenoxy-*n*-butyronitrile yields  $\delta$ -phenoxybutylamine, b. p. 140°/12 mm., and *di- $\delta$ -phenoxybutylamine*,  $(OPh\cdot[CH_2]_4)_2NH$ , a colourless, crystalline substance, m. p. 51–52°, b. p. 266°/15 mm. (*hydrochloride*, leaflets, m. p. 165°; *nitroso-derivative*, m. p. 50°; the *picrate*, *acetyl* derivative, and *benzoyl* compound could not be caused to crystallise). The secondary base is transformed by fuming hydrobromic acid to *di- $\delta$ -bromobutylamine hydrobromide*, colourless leaflets, m. p. 200°. When liberated from its salt the base immediately becomes converted into dipyrrolidinium bromide, m. p. 256–258°. Catalytic reduction of  $\delta$ -phenoxy-*n*-butyronitrile in the presence of cyclohexanol yields, in addition to the two bases just described, *cyclohexyl- $\gamma$ -phenoxybutylamine*,  $OPh\cdot[CH_2]_4\cdot NH\cdot C_6H_{11}$ ,

a colourless liquid, b. p. 177–179°/16 mm. (*picrate*, m. p. 110°; the *hydrochloride* is very hygroscopic; the *nitroso-derivative* is not crystalline).

Benzonitrile yields benzylamine and dibenzylamine, the former being very advantageously prepared if decahydronaphthalene or amyl alcohol is used as solvent. In the presence of cyclohexanol, *cyclohexylbenzylamine*, b. p. 145–147°/15 mm. (*hydrochloride*, m. p. 284°; *nitroso-derivative*, m. p. 43°; *benzenesulphonyl* compound, m. p. 90°) is also produced; the yield increases at the expense of the simple secondary base with increasing dilution of the solution. When *m*-methylcyclohexanol is used as solvent, *m*-methylcyclohexylbenzylamine, b. p. 155°/15 mm., is also produced, but the yield is relatively less than that of the lower homologue, doubtless owing to the diminished mobility of the hydroxyl group; the non-crystalline *nitroso-derivative*, the *hydrochloride*, colourless prisms, m. p. 249°, and the *hydrobromide*, m. p. 245–248°, are described.

Hydrogenation of the naphthonitriles is effected at about 190°, and leads mainly to the production of primary amines; it is remarkable that the nucleus does not appear to be attacked under these conditions.  $\alpha$ -Naphthylmethylamine has b. p. 155°/12 mm., the *hydrochloride*, m. p. 262–264°, the *picrate*, m. p. 223°, the *phenylthiocarbamide* compound, m. p. 216°, the *acetyl* derivative, colourless needles, m. p. 134°, the *benzenesulphonyl* compound, m. p. 148°, and  $\alpha$ -naphthylmethyltrimethylammonium iodide, lustrous leaflets,

m. p. 213°, are described. *Di-α-naphthylmethylamine*, m. p. 73—74°, yields a *hydrochloride*, m. p. 239°, a *picrate*, m. p. 202°, a *nitroso-derivative*, rectangular leaflets, m. p. 147°, and *di-α-naphthylmethylidimethylammonium iodide*,  $\text{NMe}_2(\text{CH}_2\text{C}_{10}\text{H}_7)_2\text{I}$ , m. p. 209—210°. *β-Naphthylmethylamine*, b. p. 148—149°/12 mm., m. p. 60°, gives a *hydrochloride*, m. p. 269°, a *picrate*, m. p. 226°, an *acetyl derivative*, m. p. 126°, and *β-naphthylmethyltrimethylammonium iodide*, colourless prisms, m. p. 168°. *Di-β-naphthylmethylamine*, n. p. 95°, yields a *hydrochloride*, m. p. 285°, a *picrate*, m. p. 126°, a *nitroso-derivative*, m. p. 132°, and *di-β-naphthylmethylidimethylammonium iodide*, m. p. 217°.

The hydrogenation of phenylacetonitrile has been studied under varied conditions. *β-Phenylethylamine* and *di-β-phenylethylamine*, colourless crystals, m. p. 28—30°, b. p. 195°/18 mm. (*picrate*, m. p. 50°, *nitroso-derivative*, m. p. 53°; *phenylthiocarbamide* compound, n. p. 113°), are the usual products. In the presence of cyclohexanol, phenylacetonitrile yields also *β-phenylethylcyclohexylamine*,  $\text{H}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_{11}$ , a liquid, b. p. 163—169°/13 mm., the *hydrochloride*, m. p. 199°, the *sulphate*, and the *picrate*, m. p. 154°, of which are also described. In the presence of benzyl alcohol, the only secondary amine which is formed is *benzyl-β-phenylethylamine*, a liquid, b. p. 186—187°/15 mm. (*hydrochloride*, m. p. 254°, *nitroso-derivative*, m. p. 142°; *benzoyl derivative*, m. p. 123°; *picrate*, m. p. 146°). Similarly, in the presence of *p*-methylbenzyl alcohol, the sole secondary base produced is *p-xylyl-β-phenylethylamine*,  $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , b. p. 191—193°/14 mm. *hydrochloride*, m. p. 238—240°; *picrate*, m. p. 139—141°).

*β-Phenylpropionitrile* is hydrogenated in the presence of decalynaphthalene or *β-phenylethyl alcohol* to *γ-phenylpropylamine*, b. p. 112—114°/18 mm., and *di-γ-phenylpropylamine*, b. p. 220—222°/18 mm. In the presence of benzyl alcohol, it gives also *benzyl-γ-phenylpropylamine*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , a liquid which forms a *hydrochloride*, m. p. 184—185°, and a non-crystalline *nitroso-derivative*.

*o*-Toluenitrile is transformed into *o*-xylylamine and *di-o-xylylamine*,  $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$ , b. p. 190°/16 mm. (*hydrochloride*, m. p. 102°; *picrate*, m. p. 133°). *Di-m-xylylamine*, b. p. 189—191°/14 mm., gives a *hydrochloride*, m. p. 199°, and a *benzoyl derivative*, m. p. 100°. *Di-p-xylylamine*, b. p. 220°/13 mm., solidifies when cooled in ice.

*α-Tetrahydronaphthonitrile* is reduced in tetrahydronaphthalene solution to *ar-α-tetrahydronaphthylmethylamine*,  $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{NH}_2$ , b. p. 150°/14 mm. (yield 70%) and *di-ar-α-tetrahydronaphthylmethylamine*, m. p. 93° (*hydrochloride*, m. p. 212°; *nitroso-derivative*, m. p. 90—91°). Similarly, *β-tetrahydronaphthonitrile* yields *tetrahydronaphthylmethylamine*, b. p. 147°/11 mm., and *di-tetrahydronaphthylmethylamine*, b. p. 265—267°/11 mm. (*hydrochloride*, m. p. 245°; *benzoyl derivative*, m. p. 241—242°; *nitroso-compound*, m. p. 76°). The yield of primary amine from the nitrile is much smaller than from the *α*-compound, whilst that of the secondary base is much greater.

H. W.

qq\*

**Reductions with Co-operation of Metallic Hydrides.** KARL KINDLER (*Ber.*, 1923, 56, [B], 2063—2064).—Evidence is adduced to show that cathodic reduction is not entirely attributable to cathodic over-voltage but also to the intermediate formation of metallic hydrides.

[With Ö. GIESE.]—The yield of  $\beta$ -phenylethyldimethylamine obtained by the electrolytic reduction of phenylacetodimethylamide at a lead cathode is greatly increased by the addition of antimony pentoxide or arsenious oxide to the cathode solution; the action is attributed to the formation of arsine and stibine, respectively.

H. W.

**Slow Formation of a Definite Compound in Mixed Crystals.** PAUL PASCAL (*Compt. rend.*, 1923, 177, 587—589).—When mixtures of benzylideneaniline and anisylideneaniline are slowly cooled, a slight cloudiness appears at a temperature ( $t$ ) just before rapid solidification sets in, a similar result being obtained by slow heating of the solidified mixture. By plotting concentration of the two components against  $t$ , it is seen that they form a compound (2:1), m. p. 33.5°, with partial dissociation. Whereas the solidification temperature curves are smooth, with a minimum at 21—23°, the temperature-concentration curve has a well-defined maximum (33.5°), the eutectics lying at 27.5° and 25.5° for 70% and 40% of benzylideneaniline, respectively. The cloudiness is apparently not due to the formation of an anisotropic liquid.

E. E. T.

**New Secondary Bases in the Indene Series.** CH. COURTOT and A. DONDELINGER (*Compt. rend.*, 1923, 177, 536—538).—1-Bromoindene reacts at the ordinary temperature with aniline to give *phenylindanylamine*, yellowish-brown leaflets, m. p. 74—75°. The reactivity of this bromine atom (cf. Grignard and Courtot, A., 1912, i, 250) has previously been ascribed to the contiguity of the ethylenic linking, but it is now found that Weisgerber's 1-chloroindane (A., 1911, i, 623) reacts readily at the ordinary temperature with aniline, *p*- and *o*-toluidines and xylidine, and at 50—60° with *m*- and *p*-nitroanilines, the following compounds being so prepared: *Phenylindanylamine*, m. p. 40—41°, b. p. 202—203°/15 mm., *p*-tolylindanylamine, m. p. 64—65°, *o*-tolylindanylamine, m. p. 71°, *xylindanylamine*, b. p. 218°/17 mm., and *p*-nitrophenylindanylamine, yellow, m. p. 126—127°.

1-Bromoindene and 1-chloroindane react with phenols in the cold with production of hydrogen chloride, and, presumably, of the corresponding ethers.

E. E. T.

**Preparation of N-Mono- and Di-carboxylic Acid Esters of Unsymmetrically Substituted Alkylenediamines.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (*Brit. Pat.* 203608).—The above esters are prepared by the interaction, in water or an organic solvent (ether, benzene), of an ester of a halogenated formic acid and an unsymmetrically substituted alkylenediamine. With equimolecular proportions, a monocarboxylic ester is obtained, whilst a mixture of 2 mols. of formic ester with 1 mol. of diamine (or equimolecular proportions of monocarboxylic ester and diamine)

yields a dicarboxylic ester. The free bases are oils which cannot be distilled under atmospheric pressure, and are insoluble in water but soluble in most organic solvents. Of their salts, those formed with halogen acids are readily soluble in water, whilst some dissolve also in organic solvents. Of the new compounds, which find therapeutic application, the preparation of the following is described: *Benzyl diethylaminoethylcarbamate*: a nearly odourless oil, b. p.  $127^{\circ}/0.015$  mm., giving a crystalline *hydrochloride* melting at  $105-106^{\circ}$ . The corresponding *dimethylamino-ester* is a viscid, clear oil, the *hydrochloride* of which is syrupy and hygroscopic. *Phenylethyl diethylaminoethylcarbamate* is a colourless, nearly odourless oil, b. p.  $147^{\circ}/0.025$  mm.; the *hydrochloride* forms an amorphous, hygroscopic mass. *Phenylethyl piperidyl-N-ethylcarbamate*, viscid, clear oil, b. p.  $152^{\circ}/0.015$  mm.; the *hydrochloride* melts indefinitely at  $60-75^{\circ}$ . *Menthyl diethylaminoethylcarbamate* is an oil, b. p.  $142^{\circ}/0.015$  mm.; the *hydrochloride* is a very viscid oil, boiling, with partial decomposition, at about  $170^{\circ}/0.02$  mm.; the *hexahydrobenzyl ester* is a viscous, clear oil, b. p.  $150^{\circ}/0.05$  mm.; the *phenylethyl diethylaminoethyliminodicarboxylate* has b. p.  $200-202^{\circ}/0.05$  mm.

W. T. K. B.

### $\beta$ -Nitroarylhydroxylamines. II. Picrylhydroxylamine.

W. BORSCHÉ (*Ber.*, 1923, 56, [B], 1939—1943).—A continuation of previous work (this vol., i, 778).

Trinitrophenylhydroxylamine is smoothly prepared by heating a solution of trinitrophenetole in alcohol with a small excess of hydroxylamine during several hours. It crystallises in lustrous, reddish-brown, oblique prisms, m. p.  $113^{\circ}$  (decomp.). The following derivatives are described: the *sodium* compound; the *aniline* compound which is not suitable for the characterisation of the substituted hydroxylamine; the *p-toluidine* derivative,  $C_{13}H_{13}O_7N_5$ , m. p.  $122^{\circ}$  (slow decomp.);  $\alpha$ -acetyl- $\beta$ -picrylhydroxylamine,  $C_8H_2(NO_2)_3NH \cdot OAc$ , obtained by means of acetic anhydride, dark yellow needles, m. p.  $130^{\circ}$ ;  $\alpha$ -benzoyl- $\beta$ -picrylhydroxylamine, thin red leaflets, m. p.  $167^{\circ}$  (decomp.). Trinitrophenylhydroxylamine is readily reduced to 1:2:3:5-tetraminobenzene, but its oxidation to 2:4:6-trinitro-1-nitrosobenzene has not yet been effected. It is converted by fuming nitric acid ( $d < 1.54$ ) into 1:2:3:5-tetranitrobenzene, coarse, pale yellow needles, m. p.  $125-126^{\circ}$ , which is readily converted by dilute sodium hydroxide solution or by nitric acid ( $d 1.395$ ) into picric acid, by aqueous or alcoholic ammonia into picramide, and by aniline into 2:4:6-trinitrodiphenylamine.

The preparation of 2:4:6-trinitrophenylhydroxylamine by the action of picryl chloride on hydroxylamine hydrochloride in boiling alcoholic solution has been described in the literature; a further examination of the change has shown that the product is a mixture of picric acid and picramide, but it is not certain whether these substances are formed independently.

H. W.

**Use of the Salts of the Arylsulphonhalogenoamides in the Estimation and Iodination of Phenols.** ELWYN ROBERTS (*T.*, 1923, 123, 2707—2712).

**Nitrosation of Phenols. I. 3-Chloro-4-nitrosophenol and its Conversion into Two Isomeric Chloroquinonemono oximes.** HERBERT HENRY HODGSON and FRANCIS HARRY MOORE (T., 1923, 123, 2499—2507).

**Derivatives of 3:5-Dinitrophenol. II.** GUSTAV HELLER (Ber., 1923, 56, [B], 1873—1876).—A continuation of previous work (A., 1909, i, 567).

[With HANS GEORGI.]—2:3-Dibromo-5-nitrophenol, needles, m. p. 106° (the sodium derivative, golden-yellow leaflets, is described), is prepared by diazotising 2-bromo-5-nitro-3-aminophenol and treatment of the diazonium salt with hydrobromic acid and copper powder. It is reduced by ferrous sulphate and ammonia to 2:3-dibromo-5-aminophenol, pale yellow needles, m. p. 133°, which undergoes resinification when subjected to diazotisation. 2:4:6-Tribromo-3:5-diaminophenol crystallises in pale yellow needles, m. p. 138°. 2:5-Dinitro-3-acetamidophenol, pale yellow needles, m. p. 223° (decomp.), is obtained by the action of nitric acid (*d* 1.4) on 5-nitro-3-acetamidophenol in the presence of glacial acetic acid.

3-Nitro-5-acetamidoanisole crystallises in colourless needles, m. p. 201°; it is converted by hydrochloric acid into 3-nitro-5-aminoanisole. The latter substance is transformed by bromine in glacial acetic acid solution into 2-bromo-5-nitro-3-aminoanisole, pale yellow needles, m. p. 156—157° (hydrobromide, colourless needles, m. p. 204°), and 2:4:6-tribromo-5-nitro-3-aminoanisole, long, pale brown needles, m. p. 113°. 2-Bromo-5-nitro-3-aminoanisole is converted by diazotisation and subsequent treatment of the diazonium salt (which does not couple directly with an alkaline solution of  $\beta$ -naphthol) with hydrobromic acid and copper powder into 2:3-dibromo-5-nitroanisole, pale brown needles, m. p. 121°, which is reduced by cautious treatment with zinc dust and hydrobromic acid in glacial acetic acid solution to 2:3-dibromo-5-aminoanisole, pale yellow needles, m. p. 244—245°. The latter substance is converted through the diazo-compound into 5:6-dibromoresorcinyl 1-methyl ether, brown crystals, m. p. 108°. If the diazotised solution of bromonitroaminoanisole is diluted with water, warmed on the water-bath until evolution of gas ceases and subsequently cooled in ice, 5-nitroanisole-2:3-quinone-3-diazide, ochre-coloured needles, decomp. 172—173°, separates.

[With MAX KAMMANN.]—2-Bromo-5-nitro-3-aminophenol is converted through the corresponding diazo-compound into 2-bromo-5-nitroresorcinol, orange-yellow needles, m. p. 201° (slight decomp.). H. W.

**Electrolytic Preparation of *p*-Aminophenol.** J. C. WARNER and O. W. BROWN (J. Physical Chem., 1923, 27, 652—673).—The electrolytic reduction of *p*-nitrophenol has been investigated under various conditions. It is shown that lead is superior to copper as cathode material in this reduction, since lead cathodes permit the use of higher current densities during the reduction. An electrolyte containing sodium hydroxide gives

higher current efficiencies and higher material yields of *p*-aminophenol than electrolytes containing sodium carbonate, sodium hydrogen carbonate, or sulphuric acid. With a copper or a lead cathode, the highest current efficiencies and material yields are obtained with an electrolyte containing about 8% of sodium hydroxide. At a copper cathode, the highest current efficiencies and material yields are obtained when a current density of 1–2 amperes per sq. dm. is used. The most favourable concentration of *p*-nitrophenol in the cathode liquor is 2.0–3.0 g. in 100 c.c. of solution. With a current density of 4.0 amperes per dm.<sup>2</sup>, the most favourable temperature for the reduction is 65–75°. With a current density of 10 amperes per dm.<sup>2</sup>, the reduction is best effected near to the boiling point. When a solution of 10 g. of *p*-nitrophenol in 400 c.c. of 8% sodium hydroxide is reduced at a copper cathode with a current density of 2.0 amperes per dm.<sup>2</sup> at 72–74°, a theoretical current efficiency is obtained as long as the concentration of *p*-nitrophenol does not fall below 1.0 g. in 100 c.c., and the material yield increases as the number of ampere-hours is increased until 10% in excess of the theoretical amount of current is used. The use of a larger excess of current causes no further increase in the material yield. *p*-Aminophenol of high purity (99.0–99.5%) can be obtained from alkaline solutions of the amine by neutralising with sulphuric acid in the presence of sodium hydrogen sulphite, filtering, washing with water, and drying in a vacuum. The *p*-aminophenol remaining in the mother-liquor after precipitation with sulphuric acid can almost all be recovered by making the mother-liquor slightly acid, evaporating to dryness on a steam-bath, and extracting the dry residue with small portions of boiling absolute alcohol. On keeping, alkaline *p*-aminophenol solutions decompose quite rapidly. If small quantities of sodium hydrogen sulphite are added this decomposition is prevented. J. F. S.

***o*-Chloro-*p*-methylaminophenol Sulphate, a New Photographic Developer.** WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, 45, 2192–2194).—*o*-Chloro-*p*-nitrophenol has m. p. 110° (cf. Kollrepp, A., 1886, 1018); it is reduced by means of sodium hyposulphite and sodium hydroxide in boiling aqueous solution to *o*-chloro-*p*-aminophenol, white needles, m. p. 150–151°. When this aminophenol is treated in hot, aqueous alkaline solution with formaldehyde in the presence of an excess of zinc dust, methylation of the amino-group occurs; *o*-chloro-*p*-methylaminophenol sulphate, slender, white needles, is isolated from the product by adding sulphuric acid. It gives a red coloration, changing to deep purple, with ferric chloride solution. Both this compound and the hydrochloride of the unmethylated aminophenol are good photographic developing agents, but the former is the better, being equal to, but not better than, *p*-methylaminophenol sulphate (metol). W. S. N.

**Preparation of *p*-Aminothymol.** A. C. GRAYBEAL and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1922, 11, 252–255; from *Chem. Zentr.*, 1923, i, 1618).—In modification of Wallach's method

(A., 1895, i, 546), *p*-aminothymol is prepared from *d*-limonene by way of the nitrosochloride. *d*-Limonene nitrosochloride is obtained by acting on limonene with freshly prepared ethyl nitrite in acetic acid-ethyl alcohol solution with gradual addition of strong hydrochloric acid. Carvoxime is obtained by treatment of the nitrosochloride with alcoholic potash, and changed into *p*-aminothymol by Wallach's method.

G. W. R.

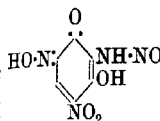
**C-Alkylation (Nucleus Alkylation) of Phenols.** L. CLAISEN (*Z. angew. Chem.*, 1923, **36**, 478—479).—The reaction between alkyl halides and the sodium derivatives of monohydric phenols of the benzene and naphthalene series results in O-alkylation when the medium is methyl or ethyl alcohol (also acetone, as a rule), whereas in non-dissociating media, *e.g.*, benzene or toluene, C-alkyl derivatives preponderate. Unsaturated radicles (*e.g.*, allyl, cinnamyl) are more easily introduced into the nucleus than saturated radicles, and the substituent enters in the ortho-position to the hydroxyl, provided this is unsubstituted. The following substituted phenols were prepared. Allylphenol: a yield of more than 90% of the ether is obtained from allyl bromide and alcoholic sodium phenoxide, whilst, in benzene or toluene, 70% of the C-allylphenol (including a little diallylphenol) is formed. Allyl-*p*-cresol: the proportions are as in the foregoing; by repeating the process with *o*-allyl-*p*-cresol, a good yield of *o*:*o*-diallyl-*p*-cresol is obtained. *o*-( $\alpha$ : $\gamma$ -Dimethylallyl)-*p*-cresol: a colourless oil, b. p. 134—136°/13 mm., giving an alkali-insoluble isomeride, b. p. 244°, when treated with acid. *o*-Cinnamylphenol: in alcoholic solution the ether (m. p. 65—66°) is exclusively formed, whereas in benzene the product is almost exclusively monocinnamylphenol (crystals, m. p. 56°, b. p. 214°/12 mm.). *o*-Cinnamyl-*p*-cresol: a thick oil, b. p. 218—220°/13 mm., giving a phenylcarbamate melting at 124.5—125°. *o*-Benzylphenol: colourless crystals, m. p. 21°, b. p. 312°/760 mm. *o*-Benzylguaiacol: the ether is the main product, even in benzene solution; the C-substituted phenol melts at 38° and boils at 195°/13 mm. *o*-Benzyl- $\alpha$ -naphthol: obtained, in 50% yield, as colourless needles, m. p. 73.5—74°, b. p. 237—240°/13 mm. *o*-Benzyl- $\beta$ -naphthol: obtained, in 60—70% yield, as a crystalline mass, m. p. 111—112°, which is probably identical with the compound obtained by Bakunin and Altieri (*cf.* A., 1904, i, 313) from  $\beta$ -naphthol, benzyl chloride, and zinc; the acetyl and benzoyl derivatives melt at 65—65.5° and 97° respectively.

W. T. K. B.

**4-Nitro-2-aminoresorcinol and 2-Nitro-4-aminopyrocatechol.** GUSTAV HELLER, PAUL LINDNER, and HANS GEORGI (*Ber.*, 1923, **56**, [B], 1868—1872).—Heller and Sourlis (A., 1910, i, 749) have described the production of a stable primary nitrosoamine by the action of nitrous acid on 2-nitro-4-aminoresorcinol; a similar compound has now been isolated from the isomeric 4-nitro-2-aminoresorcinol.

2:4-Dinitroresorcinol, dissolved in glacial acetic acid, is reduced

by the calculated quantity of stannous chloride and hydrochloric acid, and the product is converted by acetic anhydride into 4-nitro-2-acetamidoresorcinol, long, pale yellow needles, m. p. 213°, which is hydrolysed by concentrated hydrochloric acid to 4-nitro-2-amino-



resorcinol, red needles, m. p. 182° (the hydrochloride, which darkens above 225°, is described). The amine is transformed by nitrous acid into 5-nitro-3-nitrosoamino-4-hydroxy-o-quinoneoxime (annexed formula), small, yellow, hexagonal rods; the substance is not converted by hydrochloric acid into a diazonium compound which can undergo coupling, whilst also chlorine cannot be introduced by means of Gattermann's copper powder.

The constitution of 4-nitro-2-aminoresorcinol is established by the conversion of 2-aminoresorcinol into 2-acetamidoresorcinyldiacetate, colourless needles, m. p. 104°, which is subsequently transformed into 4-nitro-2-acetamidoresorcinyldiacetate, almost colourless plates, m. p. 123°; the latter compound is hydrolysed to 4-nitro-2-aminoresorcinol, m. p. 182°, which is identical with the product described above.

2-Nitro-4-aminopyrocatechol is conveniently prepared by the partial reduction of 2:4-dinitropyrocatechol by stannous chloride. The constitution of the compound is established by the observation that 4-aminopyrocatechol is converted by acetic anhydride and sodium acetate into 4-acetamidopyrocatechyl diacetate, colourless needles, m. p. 198°, which is nitrated to 6-nitro-4-acetamidopyrocatechyl diacetate, almost colourless needles, m. p. 207°. The nitro-aminopyrocatechol obtained by the hydrolysis of this compound is identical with that derived from 2:4-dinitropyrocatechol. H. W.

### The Moderated Bromination of Organic Compounds.

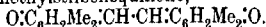
KARL W. ROSENKUND, W. KUHNHENN, and W. LESCH (*Ber.*, 1923, 56, [B], 2042—2044; cf. Rosenmund and Kuhnenn, this vol., i, 782).—Further examples of the authors' method of bromination are cited. Generally, bromine is added to a solution of quinoline sulphate and the compound to be brominated in glacial acetic acid, but in some cases quinoline hydrochloride is to be preferred. When this process leads to perbromination, a solution of quinoline sulphate and bromine in glacial acetic acid is first prepared and then added to the substance to be brominated.

The following examples are described in detail: *Bromoacetylpyrogallol*,  $\text{COMe}\cdot\text{C}_6\text{H}_3\text{Br}(\text{OH})_3\cdot\text{H}_2\text{O}$ , long needles, m. p. 186°, from acetylpyrogallol (bromoacetylpyrogallyl triacetate has m. p. 108°); *Bromoacetylresorcinol*,  $\text{COMe}\cdot\text{C}_6\text{H}_3\text{Br}(\text{OH})_2$ , colourless needles, m. p. 139°; *Bromochloroacetylpyrocatechol*,  $\text{C}_6\text{H}_4\text{O}_3\text{ClBr}$ , small, colourless needles, m. p. 137°; *3-Bromotyrosine*,  $\text{C}_9\text{H}_{10}\text{O}_3\text{NBr}\cdot 2\text{H}_2\text{O}$ , m. p. 223° (decomp.).

In reply to the criticisms of Krause (this vol., i, 891; cf. A., 1918, i, 415), it is pointed out that identical results are not obtained by bromination in pyridine solution and by the authors' method.

H. W.

**The Dehydrogenation of Mesitol.** STEFAN GOLDSCHMIDT and HANNS BERNARD (*Ber.*, 1923, 56, [B], 1963—1967).—Porter and Thurber (A., 1921, i, 505) have described the isolation of a red, crystalline substance, m. p. 50°, by the oxidation of a solution of mesitol in benzene by silver oxide, which they have considered to be derived by the combination of a molecule of mesitol with a second molecule of the same substance which has been oxidised in such a manner as to contain either univalent oxygen or tervalent carbon. This conception appears so improbable to the authors that they have repeated the work and thus drawn the conclusion that Porter and Thurber's compound has the composition  $C_{18}H_{18}O_2$  instead of  $C_{18}H_{22}O_2$  and is most probably 3:5:3':5'-tetramethylstilbenequinone,



The oxidation of mesitol by silver oxide yields the compound,  $C_{18}H_{18}O_2$ , red crystals, which decompose without melting above 200°. It is reduced by phenylhydrazine dissolved in chloroform to 4:4'-dihydroxy-3:5:3':5'-tetramethylstilbene, colourless crystals without a distinct melting point, which gives a diacetate, colourless prisms, m. p. 237°; the hydroxy-compound is converted by silver oxide into the red quinone, decomp. above 200°.

Dihydroxytetramethylstilbene is prepared by the condensation of chloral hydrate and *m*-2-xyleneol in the presence of glacial acetic acid and concentrated sulphuric acid to trichloro-4:4'-dihydroxy-3:5:3':5'-tetramethyldiphenylethane,  $CCl_3CH(C_6H_4Me_2OH)_2$ , m. p. 202—207° (corr.), and treatment of the latter with zinc dust in the presence of boiling alcohol. H. W.

**Studies in the Anthracene Series. VI.** EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS (T., 1923, 123, 2549—2557).

**Studies in the Anthracene Series. VII.** EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (T., 1923, 123, 2631—2642).

**The Preparation of the Isomeric Methoxybenzyl Bromides.** JOHN BALDWIN SHOESMITH (T., 1923, 123, 2698—2703).

**Application of the Grignard Reaction to some Acetylenic Compounds. I. Preparation of Diacetylenic Glycols.** FORSYTH JAMES WILSON and WILLIAM McNINCH HYSLOP (T., 1923, 123, 2612—2618).

**Catechin. V. Structurally Isomeric Catechins. M.** NIERENSTEIN (*Ber.*, 1923, 56, [B], 1877—1879; cf. Nierenstein, T., 1922, 121, 609).—It has been shown previously (*loc. cit.*) that tetramethylacacatechin,  $C_{13}H_9O(OMe)_4:(iCH):CH:OH$  can be converted into a pentamethyl derivative,  $C_{13}H_7O(OMe)_5:(iCH_2):C(OMe)$ , which is now shown to be identical with the pentamethyl derivative of catechin-*C* which occurs in small amount in cube-gambier and in Pegu catechin; it is designated isoacacatechin. The two pentamethyl derivatives can be partly demethylated, yielding, respectively, tetramethylacacatechin and tetramethylisoacacatechin.

$C_{13}H_{18}O(OMe)_4(C_2H_5)_2C\cdot OH$ , small, prismatic needles, m. p. 171—172°.

*Monoacetyltetramethylisocatechin* crystallises in small needles, m. p. 157—158°, whereas the corresponding *benzoyl* derivative has m. p. 141—142°.

H. W.

**Stereoisomeric 1-Phenylcyclohexane-1 : 2-diols.** S. NAMETKIN and N. IVANOV (*Ber.*, 1923, 56, [B], 1805—1807).—The oxidation of 1-phenyl- $\Delta^1$ -cyclohexene occurs in a manner closely analogous to that of 1-methyl- $\Delta^1$ -cyclohexene (Nametkin and Jarzev, this vol., i, 1081).

1-Phenylcyclohexane-1-ol is converted by treatment with sulphuric acid on the boiling water-bath into 1-phenyl- $\Delta^1$ -cyclohexene, b. p. 128°/16 mm.,  $d_4^{20}$  0.9939,  $n_D^{20}$  1.5695. The hydrocarbon is oxidised by benzoyl peroxide in ethereal solution to 1-phenylcyclohexene 1-oxide, a colourless, oily liquid, b. p. 142—143°/25 mm.,  $d_4^{20}$  1.0561,  $n_D^{20}$  1.5434, which is transformed by water at 110° into *cis*-1-phenylcyclohexane-1 : 2-diol,  $C_{12}H_{16}O_2$ , four-sided prisms, m. p. 95°. On the other hand, the hydrocarbon is oxidised by permanganate to *trans*-1-phenylcyclohexane-1 : 2-diol, a viscous liquid, b. p. 166—167°/12 mm., and  $\delta$ -benzoylvaleric acid.

H. W.

**The Chemistry of the Three-carbon System. II. Tautomeric Nitriles and Cyano-esters.** STANLEY FRANCIS BIRCH and GEORGE ARMAND ROBERT KON (*T.*, 1923, 123, 2440—2448).

**Attempt to Prepare Dihydrocampholytolactone by the Aid of the Windaus "Glutaric Acid Degradation."** MARIA BREDT-SAVELSBERG (*J. pr. Chem.*, 1922, [ii], 105, 149—157).—The action of iodine and sand on silver *cis*-camphorate at 150° gives *cis*-camphoric acid, and not, as expected, dihydrocampholytolactone. Under similar conditions, *tert*-silver *sec*-methyl camphorate is partly converted into camphoric anhydride. The Windaus method for distinguishing substituted glutaric and succinic acids (A., 1921, i, 392) cannot, therefore, be applied, without possibility of error, to ring-bound dibasic acids.

W. S. N.

**Chlorination of Benzoyl Chloride. II.** EDWARD HOPE and GEORGE CLIFFORD RILEY (*T.*, 1923, 123, 2470—2480).

**The Sweetness of "Saccharin."** The Electrolytic Dissociation of *o*-Benzoylsulphimide. O. J. MAGIDSON and S. W. GORBATSCHOV (*Ber.*, 1923, 56, [B], 1810—1817).—From a consideration of the sweetness of various derivatives of "saccharin," the authors draw the conclusion that it is the "saccharin"-ion and not the molecule which causes its solutions to have a sweet taste. It is shown that, in accordance with this view, its sweetening power and molecular conductivity are affected very similarly by dilution. Similarly, the sweetness of "sodium-saccharin," or "crystallose" is depressed in the presence of other sodium-ions, exactly as would be expected in accordance with theory. "N-Saccharinacetic acid" [*o*-benzoic-sulphimidoacetic acid] was prepared

by the action of ethyl chloroacetate on "sodium saccharin," and crystallises in needles, m. p. 212—215°. It has a bitter, acid taste, and its dissociation constant ( $k=0.14 \times 10^{-4}$ ) is practically that of acetic acid.

H. H.

**The Resolution of Hydratropic Acid.** HENRY STANLEY RAPER (T., 1923, 123, 2557—2559).

**Action of Dimethyl Sulphate on Salicylic Acid, Methyl Salicylate, and o-Methoxybenzoic Acid. Sulphonation and Methylation.** L. J. SIMON and M. FRÈREJACQUE (*Compt. rend.*, 1923, 177, 533—536; cf. this vol., i, 462).—Salicylic acid, when heated with potassium methyl sulphate, gives a 40% yield of methyl salicylate, but on heating with methyl sulphate at 110—120° affords a mixture of roughly equal amounts of methyl sulphosalicylate,  $[\text{OH} : \text{SO}_3\text{H}=1 : 4]$ , and its methyl ester (Blau, A., 1897, i, 413). One mol. of methyl sulphate gives a mixture of unchanged salicylic acid and methyl sulphosalicylate, the latter also resulting by the action of either sulphuric acid or methyl sulphate on methyl salicylate. When o-methoxybenzoic acid is heated with 3 mols. of methyl sulphate, the sulphonic acid of its methyl ester, the dimethyl ester of sulphosalicylic acid, and small quantities of methyl sulphosalicylate are produced.

E. E. T.

**The Isomerism and Polymerism of Salicylides.** RICHARD ANSCHÜTZ (*J. pr. Chem.*, 1922, [ii], 105, 158—164).—The facts at present known about  $\alpha$ -disalicylide,  $\beta$ -disalicylide, tetrasalicylide, and polysalicylide are collected, classified, and discussed.

W. S. N.

**A New Method for the Resolution of Asymmetric Compounds.** A Reply. JULIUS BEREND COREN (T., 1923, 123, 2716).

**Preparations from Maleic and Fumaric Acids.** HAROLD G. ODDY (*J. Amer. Chem. Soc.*, 1923, 45, 2156—2160).—The best conditions are described for the preparation of  $\beta$ -benzoylacrylic acid (Pechman, A., 1882, 1074; Gabriel and Colman, A., 1899, i, 390) and of  $\beta$ -toluoylacrylic acid (Pechman, *loc. cit.*; Kosniowski and Marchlewski, *Chem. Zentr.*, 1906, ii, 1190) from benzene, or toluene, respectively, and maleic anhydride, in the presence of aluminium chloride. The acid prepared from toluene gives, when boiled with 10% sodium hydroxide solution, a tolyl methyl ketone, from which *p*-toluic acid is obtained by the action of cold, alkaline potassium ferrieyanide solution; hence the acid is  $\beta$ -*p*-toluoylacrylic acid. Its methyl ester forms long, colourless needles, m. p. 45.5—46°, b. p. 240—245°/115 mm. The acid reacts in the cold with concentrated hydrochloric acid to give  $\alpha$ -chloro- $\beta$ -*p*-toluoylpropionic acid, m. p. 144—144.5°, and with bromine in cold, acetic acid solution to give  $\alpha$ , $\beta$ -dibromo- $\beta$ -*p*-toluoylpropionic acid. The action of maleic anhydride on naphthalene in warm benzene

solution in the presence of aluminium chloride gives  $\beta\beta$ -*naphthoylacrylic acid*, m. p. 189—190° (silver salt, methyl ester, plates, m. p. 94—95°), which gives  $\beta$ -naphthoic acid when oxidised by means of sodium dichromate and acetic acid at 100°. In the above condensation, a second compound, m. p. 158—159°, is also formed. The use of diphenyl and maleic anhydride leads to the formation of  $\beta$ -*p*-phenylbenzoylacrylic acid, yellow needles, m. p. 167—168° (sodium salt, silver salt, methyl ester, m. p. 73·5—74°), which reacts with bromine in hot, acetic acid solution to give  $\alpha$ - $\beta$ -dibromo- $\beta$ -*p*-phenylbenzoylpropionic acid, m. p. 180—181° (white methyl ester, m. p. 120—121°), which gives *p*-phenylbenzoic acid on being fused at 160° with potassium hydroxide. Maleic anhydride and anthracene react at 60—70° in benzene solution in the presence of aluminium chloride to give  $\beta$ -*meso*-anthroylacrylic acid, colourless crystals, m. p. 261° (sodium salt, ammonium salt), which does not react with bromine in cold or hot acetic acid solution, and is unaffected by fusion at 250° with potassium hydroxide; its methyl ester forms long needles, m. p. 149·5—150°. *trans*-Di-*p*-toluoyl-ethylene has m. p. 134·5° (Conant and Lutz, this vol., i, 685, give m. p. 148°); it is changed to the *cis*-form by exposure to sunlight in acetic acid solution (cf. Conant and Lutz, *loc. cit.*). Either form is converted by means of bromine in acetic acid solution into *dibromodi-p-toluylethane*, colourless needles, m. p. 200—200·5°, which gives *p*-toluic acid when fused at 130° with potassium hydroxide. Fumaryl chloride and *m*-xylene react in the presence of aluminium chloride to give *trans-di-o*:*p*-xyloylethylene, yellow crystals, m. p. 125·5—126°, which is partly converted into the colourless *cis*-form, needles, m. p. 65—65·5°, by the action of sunlight on its methyl-alcoholic solution. Either forms give, on treatment with bromine in hot, acetic acid solution, *dibromodi-o*:*p*-xyloylethane, white needles, m. p. 145°, which is converted into *o*:*p*-dimethylbenzoic acid by the action of fused potassium hydroxide at 135°. *Di-p-phenylbenzoylethylene*, a yellow powder, m. p. 247·5—248°, is prepared by keeping a mixture of fumaryl chloride, diphenyl, benzene, and aluminium chloride; it is apparently the *trans*-form, but is not changed by the action of sunlight on its chloroform solution. It reacts with bromine in chloroform solution to give *dibromodi-p-phenylbenzoylethane*, a white solid, m. p. 218—218·5°, the structure of which is assumed. Rubidge and Qua's method (A., 1914, i, 539) for the preparation of diphenylphthalide is not applicable to the preparation of diphenylcrotonolactone from maleic anhydride. Neither can this lactone be prepared by the action of benzene and aluminium chloride on the mixed anhydride, m. p. 113—114°, of acetic acid and  $\beta$ -benzoylacrylic acid.

W. S. N.

**The Formation of 3:5-Dinitro- $\beta$ -resorcylic Acid by the Action of Concentrated Nitric Acid on Extracts of Quebracho Wood and Mimosa Bark.** HANS EINBECK and LUDWIG JABLONSKI (*Ber.*, 1923, 56, [B], 1906—1908).—3:5-Dinitro-3-resorcylic acid has been obtained by the action of nitric acid on the

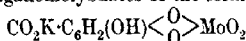
extracts of quebracho wood and mimosa bark in addition to styphnic acid (cf. Einbeck and Jablonski, A., 1921, i, 505); the former substance appears to be the precursor of the latter in the reaction. It appears, therefore, that the quebracho tannin contains the grouping shown in the annexed scheme.

[With H. SCHWABE.]—The following derivatives of 3:5-dinitro- $\beta$ -resorecylic acid are described: the *monopotassium* salt, pale yellow needles; the explosive *dipotassium* salt, pale, orange-coloured needles; the *monomethyl* ester, lustrous rodlets, m. p. 196°. H. W.

**Hetero-poly-compounds of Gallic Acid with the Anhydrides,  $\text{MoO}_3$ ,  $\text{WO}_3$ , and  $\text{UO}_3$ .** L. FERNANDES (*Gazzetta*, 1923, 53, 514–520).—With numerous organic hydroxy-acids molybdic anhydride forms compounds with a complex anion assumed to be formed by elimination of a molecule of water from the anhydride and the alcoholic hydroxyl group. This hypothesis is supported by the results obtained with gallic acid and the trioxides of the heavy elements of the sixth group of the periodic system. Thus, the intense coloration of the compounds obtained is characteristic of phenolic reactions, and the reaction occurs even better when the hydrogen of the carboxyl group is replaced by a metal, the formation of double salts being thus virtually excluded. Three series of compounds are formed, according as one, two, or three of the hydroxyls of the gallic acid are substituted by metals. Finally, cryoscopic determinations demonstrate the formation of complex anions which are only very slightly dissociated.

*Sodium*, *potassium*, and *ammonium monogallomolybdates* of the form  $\text{MoO}_2[\text{O}-\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{CO}_2\text{K}]_2$  form deep red, lustrous, scaly masses and are readily soluble in water and stable towards dilute acids.

The following digallomolybdates of the form



were prepared and analysed: *potassium*, at first red, darkening to chestnut later; *thallium*, green and amorphous; *barium*, pale chestnut; *nickel*, greenish-black and microcrystalline. The trisubstituted *potassium* compound,  $\text{MoO}_2[\text{O}-\text{C}_6\text{H}_2(\text{CO}_2\text{K})\langle\text{O}\rangle\text{MoO}_2]_3$ , forms deep chestnut, slender needles.

The gallotungstates prepared were: *Potassium monogallotungstate*,  $\text{WO}_2[\text{O}-\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{CO}_2\text{K}]_2$ , a deep chestnut, amorphous compound; *potassium digallotungstate*,  $\text{CO}_2\text{K}-\text{C}_6\text{H}_2(\text{OH})\langle\text{O}\rangle\text{WO}_2$ ; and *potassium trigallotungstate*, a brown, amorphous precipitate. The three corresponding *potassium gallouranates* were also prepared. T. H. P.

**The Isomerism of the Oximes. XIV. 3-Nitro- and 3-Bromo-*p*-dimethylaminobenzaldoximes.** OSCAR LISLE  
BRADY and RICHARD TRUSZKOWSKI (T., 1923, 123, 2434–2439).

**Certain Salts of Probable *meta*-Quinonoid Structure.**

G. RASTELLI (*Gazzetta*, 1923, 53, 485—486).—The investigations previously described (A., 1922, i, 1073) have now been extended to the *m*-nitrophenylhydrazones of benzaldehyde and tribromo-*m*-benzoquinone.

The pale yellow acetone solution of benzaldehyde *m*-nitrophenylhydrazone immediately becomes deep green on addition of sodium methoxide; in presence of a large excess of the latter, these saline compounds decompose and, if the solutions are dilute, the green colour disappears in the course of a few hours. Under similar conditions, pyruvic acid *m*-nitrophenylhydrazone exhibits only a slight green coloration which disappears almost immediately. Like many quinones and also the salts of the corresponding para- and ortho-derivatives, the alkali salt of benzaldehyde-*m*-nitrophenylhydrazone exhibits a pronounced absorption band at about  $N=2000$ . The same position is occupied by the principal band for tribromo-*m*-benzoquinone *m*-nitrophenylhydrazone, which is, however, dimeric. A quinonoid structure must be assumed for the alkali salts of these hydrazones.

T. H. P.

**Synthesis of an Aldehyde having an Odour of Vervain :**

*iso*Propyl-*p*-ethanalbenzene [*p*-Cymylacetaldehyde]. L. BERT (*Compt. rend.*, 1923, 177, 550—551).—*p*-Cymylacetaldehyde,  $C_6H_4PrCH_2CHO$ , was prepared by condensing magnesium cymyl chloride with ethyl orthoformate and hydrolysis of the resulting product with sulphuric acid, the aldehyde being separated by means of its bisulphite compound. It is a pale yellow liquid, less dense than water, b. p.  $243^\circ$ , and has a strong odour of vervain. Although a reducing agent, it is without action on Fehling's solution. The semicarbazone, m. p.  $181^\circ$ , forms white spangles.

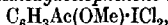
H. J. E.

**Condensation of Diphenylformamidine with Phenols. I. A New Synthesis of  $\beta$ -Resorcyaldehyde.** JOHN BALDWIN SHOESMITH and JOHN HALDANE (T., 1923, 123, 2704—2707).

**The Relation between Molecular Structure and Odour in Trisubstituted Benzenes. I. Derivatives of *p*-Methoxyacetophenone.** MARSTON TAYLOR BOGERT and LEO PATRICK CURTIN (*J. Amer. Chem. Soc.*, 1923, 45, 2161—2167).—A number of derivatives of *p*-methoxyacetophenone, containing a substituent ortho to the methoxyl radicle, have been synthesised, and shown to be odourless. Thus a trisubstituted benzene carrying osmophores in the positions 1:3:4 is not always odorous, even if sufficiently volatile.

Sodium *p*-methoxyacetophenonesulphonate, large, snow-white, fatty leaflets, is obtained from the product of the action of cold fuming sulphuric acid (30%  $SO_3$ ) on *p*-methoxyacetophenone; it reacts with methyl sulphate to give the methyl ester, a colourless liquid. *n*-Nitro-*p*-methoxyacetophenone may be obtained in 95% yield by the action of a cold ( $0^\circ$ ) mixture of concentrated nitric and sulphuric acids on *p*-methoxyacetophenone; it is reduced by means of tin and hydrochloric acid to *m*-amino-*p*-methoxyacetophenone,

large, flat, colourless, odourless, hexagonal prisms, m. p. 102° (corr.), yield 74%, *acetyl* derivative, colourless, rhombic prisms, m. p. 122.5° (corr.), *benzylidene* derivative, a solid which easily liquefies, *p-nitrobenzylidene* derivative, an amorphous solid, deep red to yellow, softens 135°, m. p. indefinite, about 160°. *m-Iodo-p-methoxyacetophenone*, yellow, feathery, odourless needles, m. p. 103.6° (corr.), is obtained from the amine by the aid of the diazo reaction; it is converted by the action of dry chlorine, in chloroform solution, into *p-methoxyacetophenone-m-iodochloride*,



small, bright yellow crystals, which is unstable, but reacts, when freshly precipitated, with 5*M*-potassium hydroxide solution to give *m-iodoso-p-methoxyacetophenone*, a greyish-white, amorphous mass (decomp. suddenly when heated), and *m-iodoso-p-hydroxyacetophenone*, long, pale yellow needles, m. p. 243° (but decomp. suddenly when rapidly heated). *m-Cyano-p-methoxyacetophenone*, slender, pale yellow, odourless needles, m. p. 159.5° (corr.), is prepared in the usual way from the amine, yield 70%; it cannot be hydrolysed to the corresponding amide or acid, and is not converted into the iminochloride by means of anhydrous methyl-alcoholic hydrogen chloride. 5-*Acetyl-2-methoxydiazobenzene perbromide*, pale yellow, flat needles, m. p. 68–70°, is immediately precipitated in almost the theoretical yield when bromine in hydrobromic acid solution is added to the diazonium chloride; it gradually decomposes on keeping. The action of ammonium hydroxide solution on an aqueous suspension of the perbromide gives 5-*acetyl-2-methoxyazidobenzene*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Ac}\cdot\text{N}_3$ , faintly pinkish-buff, long, delicate needles, m. p. 87° (decomp. corr.) (explodes if heated rapidly). 5 : 5'-*Diacetyl-2 : 2'-dimethoxydiazaminobenzene*, small, pale yellow needles, m. p. 178° (corr.), yield 95%, is obtained by diazotising the amine (above), and treating the product with the amine hydrochloride. When it is kept in an aqueous solution containing an equivalent quantity of hydrochloric acid, it is partly converted into 4-amino-5 : 5'-*diacetyl-2 : 2'-dimethoxyazobenzene*, dark red, microscopic crystals, m. p. 198–200° (corr.).

From observations on the properties and reactions of the above-mentioned compounds, the following clauses are added to V. Meyer's laws governing steric hindrance. (1) The hindering effect of an interfering group diminishes as the molecular weight of the reacting group in the ortho-position increases. (2) It also diminishes with increasing molecular weight of the foreign reacting molecule.

W. S. N.

**Derivatives of Dihydroxydiphenylsulphone.** O. HINSBERG (*Ber.*, 1923, 56, [B], 2008–2012).—A further instance of stereoisomerism analogous to that of the  $\beta$ -naphthol sulphide is described (cf. Hinsberg, A., 1919, i, 202). *p*-Dihydroxydiphenylsulphone,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , loses one molecular proportion of water when heated at 250–270° and yields a mixture of isophenyl-*p*-benzoquinonylsulphoxide,  $\text{C}_6\text{H}_5\cdot\text{SO}\cdot\text{C}_6\text{H}_3\text{O}_2$ , and isodiphenylene-sulphidoquinone,  $\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\text{O}_2$ , slender, yellowish-brown

needles, m. p. 80–85°, which has not been separated completely into its components. The quinonoid nature of the product is established by its reaction with very approximately one molecular proportion of *p*-nitrophenylhydrazine. Treatment of the mixture with acetic anhydride and zinc dust yields *isodiacetoxydiphenyl sulphide*,  $\text{SPh}\cdot\text{C}_6\text{H}_5(\text{OAc})_2$ , small, yellow needles, m. p. 65°, and *isodiacetoxydiphenylene sulphide*,  $\text{C}_6\text{H}_4\text{--}\overset{\text{S}}{\text{C}}\text{--}\text{C}_6\text{H}_5(\text{OAc})_2$ , small, yellow crystals, m. p. 126°, which can be separated from one another by taking advantage of the difference in solubility in methyl alcohol; if the reduction is effected at the atmospheric temperature, *isodiacetoxydiphenyl sulphoxide*,  $\text{SOPh}\cdot\text{C}_6\text{H}_5(\text{OAc})_2$ , colourless crystals, m. p. 95°, can be isolated, which is also produced by the careful oxidation of the sulphide dissolved in glacial acetic acid by means of hydrogen peroxide. *isoDiacetoxydiphenylene sulphoxide* crystallises in small, yellow needles, m. p. 185°. More energetic oxidation of *isodiacetoxydiphenyl sulphide* or of the corresponding sulphoxide with hydrogen peroxide leads to the production of *isodiacetoxydiphenylsulphone*, which has not been isolated in the homogeneous condition; it is, however, shown to be distinct from the normal *diacetoxydiphenylsulphone*, leaflets or pointed prisms, m. p. 129°. H. W.

**Preparation of 1-Phenylimino-2-naphthaquinone.** SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE ST. DENIS, ANDRÉ RAOUL WAHL, and ROBERT LINTZ (Brit. Pat. 191064).—2-Hydroxy-1-phenylnaphthylamine (this vol., i, 674) is readily oxidised in alkaline solution by air or other oxidising agents to 1-phenylimino-2-naphthaquinone, a green, crystalline, very unstable substance which dissolves in solvents such as acetone or ether with a blue colour. In sulphuric acid the solution is reddish-brown. For example, 94 g. of 2-hydroxy-1-phenylnaphthylamine are dissolved in a warm mixture of 80 c.c. of sodium hydroxide solution (40° Bé.) and 700 to 800 c.c. of alcohol and the solution poured into 14 litres of ice-water and filtered. A concentrated solution of sodium hypochlorite containing the theoretical quantity of chlorine in 8–10 litres of water is then added with vigorous stirring, keeping the temperature at 5°, and controlling the reaction with starch-iodide paper. The crystalline precipitate can be purified by recrystallisation from diluted acetone or a mixture of ether and light petroleum. P. M.

**Anthraquinone as a Catalyst in the Discharge of  $\alpha$ -Naphthyl amine-claret. Sodium  $\beta$ -anthranolsulphonate.** M. BATTAGAY and PH. BRANDT (*Bull. Soc. Ind. Mulhouse*, 1923, 89, 365–375).—Reduction of anthraquinone- $\beta$ -sulphonic acid by means of sodium formaldehyde-sulphoxylate under conditions similar to those employed in textile printing for the discharge of insoluble azo-dyes, results in the formation of anthranol- and anthrone- $\beta$ -sulphonic acids which are stable and therefore do not assist the discharge process. Derivatives of anthracene- $\beta$ -sulphonic acid are not formed simultaneously. The pure sodium salts of anthranol-

and anthrone- $\beta$ -sulphonic acids were prepared, the former as yellow and the latter as almost colourless, crystalline spangles, both being stable at 130°. Sodium  $\beta$ -anthranol-sulphonate is more stable than the free acid. It yields a yellow solution in concentrated sulphuric acid and readily decolorises solutions of iodine and bromine, thereby forming anthraquinone- $\beta$ -sulphonic acid. When dissolved in warm 60% alcohol, it is partly converted into the isomeric anthrone, the conversion being completed by addition of hydrochloric acid. Sodium anthranolsulphonate readily forms a violet condensation product with *p*-nitrosodimethylaniline. It is decomposed by acids, thereby forming sodium anthraquinone- $\beta$ -sulphonate and dimethyl-*p*-phenylenediamine. Sodium anthranol- $\beta$ -sulphonate couples with diazotised *p*-nitroaniline in neutral solution, forming a simple azo-compound, orange needles. The corresponding anthrone compound couples with diazo-compounds only in the presence of sodium acetate. Sodium anthrone- $\beta$ -sulphonate is less soluble than the anthranol compound in water.

A. J. H.

**Reduction in the Anthraquinone Series.** M. BATTEGAY and HUERER (*Bull. Soc. chim.*, 1923, [iv], 33, 1094—1098).—Anthraquinone- $\beta$ -sulphonic acid is reduced in alkaline solution by means of sodium hyposulphite to anthranol- $\beta$ -sulphonic acid, and further, to anthrone- $\beta$ -sulphonic acid. It is found that both anthraquinone itself and anthraquinone- $\alpha$ -sulphonic acid behave in a similar manner, and the authors suggest that this may be a general reaction. H. H.

**Reduction Products of Hydroxyanthraquinones.** III. ARNOLD BREARE and ARTHUR GEORGE PERKIN (T., 1923, 123, 2603—2611).

**Occurrence of *l*-Menthone in Pine Oil.** A. H. GILL (*Ind. Eng. Chem.*, 1923, 15, 887).—A commercial sample of pine oil known as "apinol" was distilled under 4 mm. pressure. About 60% distilled over between 74° and 79°, and 10% between 79° and 100°. By repeated fractionation of the first fraction at atmospheric pressure two distinct fractions were isolated, one boiling at 202—203°, constituting 8% of the original oil, which was identified as optically inactive fenchyl alcohol, and the other at 208.5—209.5°, which constituted 20% of the original oil, and had an optical rotation of  $-20^{\circ} 28'$ . The latter fraction was identified as *l*-menthone by converting it into its semicarbazone (m. p. 184°). This is the first time *l*-menthone has been isolated from oils from the *Pinus* family of trees.

H. C. R.

**Camphor and Nitrophenols.** N. N. EFREMOV (*Bull. acad. Sci. Russie*, 1919, 255—286).—Nitrophenols do not form molecular compounds, as do phenols, with camphor. Photomicrographs are given for mixtures containing 20 and 70% of picric acid, styphnic acid, and nitroresorcinol, respectively. The eutectic composition, eutectic temperature, and limits of solid solution, respectively, are: *o*-nitrophenol, 45%, 11.8°, 100—92%; *m*-nitrophenol, 41.5%, 16°, 100—65% (approx.); *p*-nitrophenol, 36%,  $-2^{\circ}$ , 0—13

and 70—100% (approx.); 2:4-dinitrophenol, 30.7%, 69.3°, 93—100%; picric acid, 30.5%, 66.4°, 96—100%; 2-nitroresorcinol, 39.3%, 4.6°, 90—100%; 2:4-dinitroresorcinol, 29%, 47.2°, 0—15 and 68—100% (approx.); styphnic acid, 25.3%, 82.6°, 89—100%; " $C_6H_3(OH)_2NO_2$ ", 33.2%, 26.4°, 0—23 and 73—100% (approx.); 4-nitropyrocatechol, 38%, 25.8°, 0—8 and 86—100% (approx.).

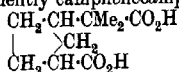
## CHEMICAL ABSTRACTS.

**Some New Constituents of Camphor Oil.** F. ROCHUSSEN (*J. pr. Chem.*, 1922, [ii], 105, 120—136).—Ethylguaiaicol,  $C_6H_3Et(OMe)OH$ , b. p. 94—95°/5 mm.,  $d^{20}_4$  1.0473,  $n^{20}_D$  1.53340, has been isolated from the phenol fraction of camphor oil; its crystalline benzoate has m. p. 59°. The acid fraction contains  $\alpha$ -hexoic acid, which is isolated as its ethyl ester, b. p. 55—56°/10 mm., and  $\alpha$ -citronellic acid. The latter has b. p. 116—118°/3 mm., 121°/3.5 mm., or 126°/4 mm.,  $d^{20}_4$  0.9557,  $n^{20}_D$  +0° 51', 200 mm. (? due to impurity),  $n^{20}_D$  1.46231,  $n^{20}_D$  1.46062, amide, m. p. 88—90°, ethyl ester, b. p. 86°/3 mm. On oxidation by means of potassium dichromate in boiling sulphuric acid solution it gives acetone and  $\beta$ -methyladipic acid, whilst  $\beta$ -methylhexoic acid is formed by fusion at 250—300° with potassium hydroxide and a little water.  $\alpha$ -Citronellic acid is converted by the action of boiling dilute sulphuric acid into a lactone, b. p. 102—103°/4.5 mm., which gives, on hydrolysis, a mixture of unsaturated and hydroxy-acids, as shown by analysis of a silver salt. The formation of this lactone is presumably preceded by a migration of the double bond.

W. S. N.

**The Bromination of Camphene; Dicumphenyl Ether and a Ring-Homologue of Camphenilone.** P. LIPP (*J. pr. Chem.*, 1922, [ii], 105, 50—64).—The action of anhydrous potassium hydroxide on boiling  $\omega$ -bromocamphene leads to the formation of a ketone (below), which may be removed in a current of steam, and of dicumphenyl ether,  $(C_{10}H_{15})_2O$ , a colourless oil, b. p. 182°/9.5 mm. (corr.), having a slight odour of geranium. This ether is unattacked by metallic sodium in boiling xylene solution, but immediately decolorises alkaline potassium permanganate solution or bromine in chloroform solution. In the latter reaction, approximately 4 atoms of halogen are absorbed. No pure product could be isolated by reducing the compound in anhydrous ethereal solution by means of hydrogen and platinum black, or by oxidation by means of potassium permanganate, but the action of chromium trioxide in cold, glacial acetic acid solution gives a ketone of the  $C_{10}$  series, the semicarbazone of which decomposes at 227—228° (corr.). The action of warm, 50% sulphuric acid on dicumphenyl ether gives camphenilanaldehyde, together with small quantities of stereoisomeric camphenilanic acids. The ketone, referred to above, is homocumphenilone (alternative formulæ annexed); it has m. p. 38—40°, b. p. 85°/14 mm. (corr.), semicarbazone, m. p. about 235° (decomp.). It

closely resembles camphenilone, but is readily attacked by alkaline potassium permanganate at 100°, with formation of an acid, m. p. 136—138° (corr.), evidently camphenecamphoric acid,



W. S. N.

**The Constituents of some Indian Essential Oils. XI. The Essential Oil from the Leaves of *Cupressus torulosa*, Don.** JOHN LIONEL SIMONSEN (*Indian For. Rec.*, 1923, 10, 1—10).—The leaves of *Cupressus torulosa*, the Himalayan cypress, yield, on distillation in steam, 0.5 to 0.8% of a pale brown oil with  $d_{20}^{20}$  0.87,  $n_D^{20}$  1.479, and  $[\alpha]_D^{20}$  +41.72°. This oil has been found to contain *d*-sabinene,  $\alpha$ -pinene, dipentene, and terpinene, together with propionic, *n*-octoic, and *n*-dodecoic acids in the free or combined state. Treatment with sulphuric acid gave, amongst other products, *trans*-terpin, from which the presence of  $\gamma$ -terpineol in the original oil is inferred. This compound has not hitherto been found in any naturally occurring essential oil, but, unfortunately, was not present in this one in sufficient quantity to permit of its isolation. In addition to the above compounds, two sesquiterpene fractions were isolated, having b. p. 195—200°/100 mm.,  $d_{20}^{20}$  0.9162,  $n_D^{20}$  1.507,  $[\alpha]_D^{20}$  -15.9°, empirical formula  $\text{C}_{15}\text{H}_{24}$ , and b. p. 205—220°/100 mm.,  $d_{20}^{20}$  0.9419,  $n_D^{20}$  1.506,  $[\alpha]_D^{20}$  -19.2°, and empirical formula  $\text{C}_{15}\text{H}_{26}\text{O}$ .  
H. H.

**The Constituents of Indian Turpentine from *Pinus longifolia*, Roxb. III.** JOHN LIONEL SIMONSEN (T., 1923, 123, 2642—2666).

**Swelling of Caoutchouc.** M. LE BLANC and M. KRÖGER (*Kolloid Z.*, 1923, 23, 168—176).—The swelling of caoutchouc in a number of organic solvents has been investigated. It is shown that the maximum swelling in a series (27) of organic solvents increases with increasing dielectric constant. Compounds containing halogens or sulphur have an increased swelling power. The velocity of vulcanisation of caoutchouc sols in different solvents shows very marked differences. With the exception of carbon tetrachloride, it is greatest in solvents containing chlorine, following these come the bromine derivatives and finally the hydrocarbons. Carbon disulphide and carbon tetrachloride solutions have the smallest velocity. At the commencement the velocity of the swelling is strongly dependent on the viscosity of the solvent, and because of this, the weakly swelling liquids have a swelling velocity many times as great as that of the strongly swelling liquids at the commencement. Carbon disulphide and mercaptan have the greatest swelling velocity; this is due largely to their strong swelling property and their low viscosity, but not entirely, for benzene at 60°, when its viscosity is much reduced, does not reach the swelling velocity of carbon disulphide. The various varieties of caoutchouc take up the solvent more rapidly the smaller the value of their maximum swelling. Many exceptions to this statement are found.

but it is strictly true in the case of bromine. The outstanding position of carbon disulphide in cold vulcanisation is due to its unusually large swelling velocity, and to the fact that every vulcanising agent is active slowly in it. Its swelling properties are inferior only to those of mercaptan; carbon tetrachloride is inferior to it in this respect, but this solvent has the advantage that vulcanisation takes place slowly in it.

J. F. S.

**Relation between Ability to form Resins and Chemical Constitution.** IV. W. HERZOG and J. KREIDL (*Z. angew. Chem.*, 1923, **36**, [64], 471—473; cf. A., 1922, i, 1168).—Further instances are given of the formation of resins from substances containing the "resinophore" group  $-C\equiv C-CO-$ . For example, citraconic anhydride heated at  $200^\circ$  in an inert gas gives a resin, and in the same way cinnamylidenemalonic acid,  $CHPh:CH:CH(CO_2H)_2$ , when heated, gives a resin believed to be the anhydride of the mono-carboxylic acid,  $(CHPh:CH:CH:CH-CO)_2O$ . Numerous other examples are quoted from the literature of the formation of resins from compounds containing this group. The formation of a resin from phenylketimine,  $NPh:C\equiv CH_2$ , leads to the inclusion of  $-N:C\equiv C<$  as a "resinophore" group. The conjugated double linking,  $-C\equiv C-C\equiv C-$ , is also regarded as a "resinophore" group, as exemplified by the  $\Delta^2$ -butadienes, etc., and so also is the group,  $>C\equiv C-CN-$ , as shown by the formation of a rubber-like substance by the polymerisation of methylallylideneamine,  $CH_2:CH:CH:NMe$ . P. M.

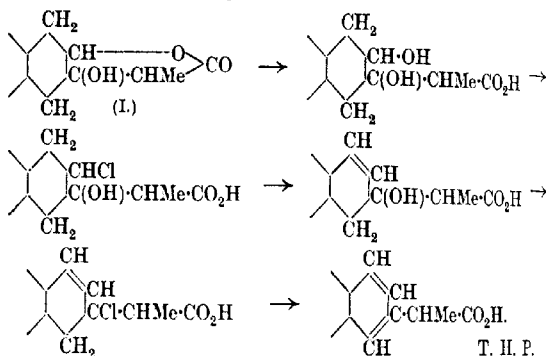
**Digitalinum Verum.** A. WINDAUS and G. BANDTE (*Ber.*, 1923, **56**, [B], 2001—2007).—The authors have commenced a systematic study of the chemistry of the cardiac poisons. The present communication is devoted to an account of digitaligenin which has been largely examined by Kiliani (A., 1914, i, 856).

The seeds of *Digitalis purpurea* are extracted with absolute alcohol and the concentrated extracts are treated with dry ether until a distinct precipitate is no longer produced. The precipitations are repeated several times and the solid is worked up for digitonin and gitonin. Digitalinum verum is isolated from the solutions by Kiliani's method and is converted into digitaligenin, needles, m. p.  $211-212^\circ$  (Kiliani, m. p.  $201-202^\circ$ ), to which the composition,  $C_{28}H_{36}O_3$ , is assigned. Acetyldigitaligenin has m. p.  $208^\circ$  (Kiliani, m. p.  $201-202^\circ$ ). Catalytic hydrogenation of digitaligenin in methyl-alcoholic solution in the presence of spongy palladium leads ultimately to the production of hexahydrodigitaligenin,  $C_{24}H_{38}O_3$ , leaflets, m. p.  $186-187^\circ$ . Acetylhexahydrodigitaligenin, long, rhombic crystals, m. p.  $154-155^\circ$ , is obtained by treating the hexahydro-compound with acetic anhydride and sodium acetate or by exhaustive hydrogenation of acetyldigitaligenin. Hexahydrodigitaligenin is oxidised by chromic acid to hexahydrodigitaligenone,  $C_{24}H_{36}O_3$ , slender needles, m. p.  $205-207^\circ$  (oxime, needles, m. p.  $205-206^\circ$ ), and therefore contains a secondary alcoholic group. It is reduced by amalgamated zinc and concentrated hydrochloric acid in the presence of glacial acetic acid to the lactone,  $C_{24}H_{38}O_2$ , long, lustrous needles, m. p.  $168-169^\circ$ .

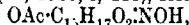
During the hydrogenation of digitaligenin a sudden drop in the rate of absorption of the gas is observed after the absorption of two molecular proportions; if the reaction is interrupted at this stage, *tetrahydrodigitaligenin*, m. p. 194°, can be isolated; the corresponding *acetate*, slender needles, has m. p. 167–168°. Kiliani's "hydrodigitaligenin" is a mixture of much tetra- and little hexa-hydrodigitaligenin.

H. W.

**Chemical Constitution of Artemisin.** P. BERTOLO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 618–622; cf. this vol., i, 1013).—The properties of artemisin are not in accord with Rimini's supposition that the oxygen atom present in addition to those of santonin occurs in the dimethylated ring as a hydroxyl group united to the carbon atom adjacent to the ketonic carbonyl of the santonin, thus:  $\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CO}\cdot$  (A., 1909, i, 115). It is certain that this oxygen atom is situated in the tetrahydrogenated ring, the most probable formula for artemisin being (I), which readily explains the formation of artemisic acid by the action of hydrochloric acid in the following manner:



**Acetyl Compound of Artemisin.** P. BERTOLO (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 76–79).—The acetyl compound of artemisin, m. p. 200° (A., 1920, i, 444), forms an *orime*,



crystallising in white needles, arranged radially, m. p. 188–189°, and a *phenylhydrazone*,  $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$ , crystallising in pink, silky needles, m. p. 145°. When hydrolysed with alcoholic potassium hydroxide, the acetyl derivative yields, not artemisin, but a crystalline compound, m. p. 220°, exhibiting acid properties.

T. H. P.

**The Constitution of Capsaicin, the Pungent Principle of Capsicum.** III. E. K. NELSON and L. E. DAWSON (*J. Amer. Chem. Soc.*, 1923, 45, 2179–2181; cf. A., 1919, i, 543; 1920, i, 380).—Capsaicin is proved to be  $\eta$ -methyl- $\Delta^8$ -nonenylvanillyl-amide,  $\text{CHMe}_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4(\text{OH})\cdot\text{OMe}$ , by the

following reactions. It is reduced, in absolute alcoholic solution by means of palladium and hydrogen, to *dihydrocapsaicin*, m. p. 65°,  $n_D^{20}$  1.510,  $n_D^{25}$  1.520,  $n_D^{30}$  1.555, which is also produced by condensing vanillylamine with  $\gamma$ -methylnonyl chloride; this demonstrates the position of the methyl group in the unsaturated acid part of the molecule. The location of the double bond is decided by the production of adipic acid and isobutyric acid, when the decenoic acid isolated by hydrolysing capsaicin is oxidised by means of cold 5% potassium permanganate solution. Dihydrocapsaicin is as pungent as capsaicin; the view of Ott and Zimmermann (A., 1922, i, 137), that this property in capsaicin and similar compounds is dependent on unsaturation in the side chain, is therefore incorrect.

W. S. N.

**A Tannin which is apparently Free from Sugar.** M. NIERENSTEIN (*Ber.*, 1923, 56, [B], 1876).—Mitchell (this vol., ii, 188) has described a commercial specimen of tannin which is optically active but does not appear to yield a sugar when hydrolysed or fermented. Further experiments have shown that the amount of dextrose produced is very slight and quite inadequate to account for the optical activity of the material which is possibly due to the presence of active leucodigallic acid.

H. W.

**[The State of Methyl-orange and Methyl-red at the Transition Point.]** A. THIEL and A. DASSLER (*Ber.*, 1923, 56, [B], 2082).—The absorption curve of methyl-red is displaced by increase in the hydrogen-ion concentration about 10  $\mu$  towards the region of shorter and not of longer wave-lengths as incorrectly stated in the earlier communication (this vol., i, 937).

H. W.

**Furfurylidene and Furfuryl Compounds of Camphor and of some cycloHexanones.** (Mlle) NELLIE WOLFF (*Ann. Chim.*, 1923, [ix], 20, 82—130).—A continuation of work previously published (cf. A., 1921, i, 514; 1922, i, 668; this vol., i, 937). The following compounds are described: *Furfurylcamphor*, colourless crystals, m. p. 65°,  $R_a$  65.45,  $R_D$  65.88,  $R_B$  66.80, prepared by the action of sodium amalgam on furfurylidene camphor and only clearly distinguishable from the latter by its optical properties; *monofurfurylcyclohexanone*, a pale yellow liquid, b. p. 136°/17 mm.,  $n_D^{20}$  1.49896,  $n_D^{25}$  1.50244,  $n_D^{30}$  1.51139, *difurfurylcyclohexanone*, colourless leaves, m. p. 53°,  $R_a$  70.14,  $R_D$  70.62,  $R_B$  73.54, obtained by reduction of the corresponding mono- and di-furfurylidene compounds, respectively; *2-furfuryl-4-methylcyclohexanone*, a yellow oil, b. p. 148—150°/20 mm.,  $n_D^{20}$  1.49464,  $n_D^{25}$  1.49812,  $n_D^{30}$  1.50762; *2:6-difurfuryl-4-methylcyclohexanone*, colourless needles, m. p. 52°,  $R_a$  74.48,  $R_D$  75.09,  $R_B$  76.69, by reduction of the furfurylidene derivatives *2-furfurylidene-5-methylcyclohexanone*, yellow crystals, m. p. 43°,  $R_a$  57.30,  $R_D$  58.93,  $R_B$  61.51; *2:6-difurfurylidene-5-methylcyclohexanone*, yellow crystals, m. p. 68°,  $R_a$  89.97,  $R_D$  92.65,  $R_B$  99.84. Optically active isomerides of the two last-named substances were prepared as condensation products of active 5-methylcyclohexanone, but these derivatives are of opposite sign to that of

the hexanone used. *Active 2-furfurylidene-5-methylcyclohexanone* forms yellow crystals, m. p.  $43^{\circ}$ ,  $R_a$  58-23,  $R_D$  58-95,  $R_B$  60-89,  $[\alpha]_D^{25} -11^{\circ} 47'$ ; *active 2:6-difurfurylidene-5-methylcyclohexanone*, yellow crystals, m. p.  $68^{\circ}$ ,  $R_a$  92-46,  $R_D$  93-93,  $R_B$  103-17,  $[\alpha]_D^{25} -172^{\circ} 38'$ . Active and inactive isomerides of both substances yield the furfuryl derivative on reduction; *2-furfuryl-5-methylcyclohexanone* is a yellow oil, b. p.  $142-143^{\circ}/17$  mm.,  $d_4^{25} 1.0419$ ,  $n_D^{25} 1.49530$ ,  $n_D^{25} 1.49897$ ,  $n_D^{25} 1.50876$ , the constants for the active form being  $d_4^{25} 1.0370$ ,  $[\alpha]_D^{25} -5^{\circ} 13'$ ,  $n_D^{25} 1.48864$ ,  $n_D^{25} 1.49290$ ,  $n_D^{25} 1.50069$ ; *2:6-difurfuryl-5-methylcyclohexanone*, a yellow liquid, b. p.  $196-200^{\circ}/16$  mm.,  $R_a$  74-70,  $R_D$  75-10,  $R_B$  76-98; the active form has b. p.  $202-204^{\circ}/16$  mm.,  $[\alpha]_D^{25} -6^{\circ} 37'$ ,  $R_a$  74-66,  $R_D$  75-17,  $R_B$  76-44.

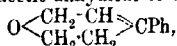
A study of the optical properties of the substances prepared in the course of the work shows that those in which a double bond occurs between the two rings give unusually high values for molecular refraction and dispersion, the values given by the substances obtained on hydrogenation of the double bond being normal.

H. J. E.

**Tetrahydro- $\gamma$ -pyrones. II.** W. BORSCHKE and K. THIELE (*Ber.*, 1923, **56**, [B], 2012-2015; cf. Borsche and Mehner, A., 1915, i, 574).—The hydrogenation of 4-pyrone and 2:6-dimethyl-4-pyrone is effected as described in the previous communication: the operation is particularly tedious in the case of the dimethyl derivative.

The following compounds are prepared from tetrahydro-4-pyrone: the *oxime*, long, colourless needles, m. p.  $87-88^{\circ}$ , which is reduced by aluminium amalgam in the presence of moist ether to the corresponding *amine*, a colourless liquid without a definite boiling point (the very hygroscopic *hydrochloride*, the *benzoyl* derivative, prisms, m. p.  $172^{\circ}$ , and the *carbamate*,  $C_6H_{12}O_2N_2$ , colourless leaflets, m. p.  $226-227^{\circ}$ , are described). With magnesium phenyl bromide,

tetrahydro-4-pyrone gives the compound,  $O \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CPh} \cdot \text{OH}$ , colourless, lustrous needles, m. p.  $103-104^{\circ}$ , which is smoothly dehydrated by boiling acetic anhydride to the substance,



colourless leaflets, m. p.  $61-62^{\circ}$ , which rapidly becomes converted into a colourless resin when preserved. Tetrahydro-4-pyrone is oxidised by potassium permanganate in alkaline solution to the *dicarboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , colourless needles, m. p.  $93-94^{\circ}$  (*di-ethyl* ester, a colourless, mobile liquid, b. p.  $247-249^{\circ}$ ).

2:6-Dimethyltetrahydro-4-pyrone gives an *oxime*, colourless needles, m. p.  $82-83^{\circ}$ , b. p.  $210-220^{\circ}/760$  mm. (*benzoyl* derivative, coarse, colourless prisms, m. p.  $93^{\circ}$ ); it is reduced by aluminium amalgam to the corresponding *amine*, which is isolated as the very hygroscopic *hydrochloride* and the *benzoyl* derivative, small, colourless needles, m. p.  $189-190^{\circ}$ . Unlike tetrahydro-4-pyrone, the dimethyl derivative is readily reduced to 2:6-dimethyl-

*etrahydropyran-4-ol*,  $O\langle\begin{smallmatrix} CHMe\cdot CH_2 \\ CHMe\cdot CH_2 \end{smallmatrix}\rangle CH\cdot OH$ , colourless needles, n. p. 48—49°, b. p. 190°/atmospheric pressure. 2 : 6-Dimethyl-tetrahydro-4-pyrone is converted by magnesium methyl iodide into 2 : 4 : 6-trimethyltetrahydropyran-4-ol,  $O\langle\begin{smallmatrix} CHMe\cdot CH_2 \\ CHMe\cdot CH_2 \end{smallmatrix}\rangle CMe\cdot OH$ , b. p. 36—38°/18 mm., which is transformed by boiling acetic anhydride into the corresponding *acetate*, a pale yellow liquid, b. p. 95—100°/16 mm.; with magnesium phenyl bromide it yields 4-phenyl-2 : 6-dimethyltetrahydropyran-4-ol,  $O\langle\begin{smallmatrix} CHMe\cdot CH_2 \\ CHMe\cdot CH_2 \end{smallmatrix}\rangle CPh\cdot OH$ , colourless prisms, m. p. 101—102°, b. p. 152—156°/14 mm., which is dehydrated by boiling acetic anhydride to the compound,  $\langle\begin{smallmatrix} CHMe\cdot CH \\ CHMe\cdot CH_2 \end{smallmatrix}\rangle CPh$ , a colourless liquid, b. p. 133—136°/12 mm. The latter compound is rapidly hydrogenated in the presence of colloidal palladium to the saturated substance,  $O\langle\begin{smallmatrix} CHMe\cdot CH_2 \\ CHMe\cdot CH_2 \end{smallmatrix}\rangle CHPh$ , a colourless liquid, b. p. 125—127°/13 mm. H. W.

**Pyranhydrones. IV.** WILHELM SCHNEIDER (*Annalen*, 1923, 332, 297—318).—[With ALBERT ROSS.]—The dull red precipitate, obtained by the action of sodium acetate solution on 2 : 6-diphenyl-4-methylpyrylium bromide in faintly acid solution (Schneider and Ross, A., 1922, i, 1171), is 2 : 6-diphenyl-4-methylpyranhydron; it is prepared in a granular, bluish-red, somewhat purer form, m. p. 90—105° (sinters about 55°), by the addition of saturated sodium acetate solution to a solution of the bromide in glacial acetic acid. The more pure product loses, when heated in a vacuum, approximately 1 mol. of water, whilst the less pure material, which is already partly dehydrated, loses about half that amount; in either case a methylenepyran,  $C_{18}H_{14}O$ , is obtained. Further, the fission of the pyranhydron, by solution in glacial acetic acid (cf. Schneider and Meyer, A., 1921, i, 680), leads to two products, one of which gives a perchlorate, whilst the other does not form salts.

[With HANS JACOBI.]—It is not possible to obtain a pyranhydron by the action of concentrated sodium acetate solution on 2 : 4 : 6-trimethylpyrylium perchlorate, or on a cold ethereal solution of the chloride.

4-Phenyl-2 : 6-dimethylpyrylium iodide (cf. Baeyer and Piccard, A., 1911, i, 901) is obtained by the action of potassium iodide in concentrated hydrochloric acid solution on a cold solution, obtained from the action of dimethylpyrone in anisole solution on an ethereal solution of magnesium phenyl bromide. The iodide exists in two forms, (a) ciliate clusters of slender, yellow needles, (b) red rhombs, of which the latter is the more stable; either form has m. p. 203°. A *periodide*,  $C_{18}H_{14}OI_2$ , m. p. 126—128°, is also formed, and separates as dark brown flocks. When saturated sodium acetate solution is added to a well-cooled solution of the iodide in dilute acetic acid, and the mixture kept at -10°, 4-phenyl-2 : 6-dimethylpyranhydron gradually separates in dirty violet-red flocks; it passes on drying to

a vitreous, violet mass, which may be ground to a chocolate-coloured powder, m. p. about 80°, sinters at 60°, decomp. 140°. The colour of this compound in alcoholic solution disappears on warming, and deepens on cooling.

4-*p*-Anisyl-2 : 6-dimethylpyrylium iodide is prepared in the usual way from dimethylpyrone and the Grignard reagent from *p*-bromo-anisole; it forms compact, brown crystals having a violet, metallic lustre, m. p. 215°; a yellow modification appears when a hot, saturated, alcoholic solution is suddenly cooled, this being only slowly reconverted into the more stable form. The picrate forms small, slender, yellow needles, m. p. 186°. The corresponding pyranhydrone is a reddish-brown, violet-tinted, resinous mass, which cannot be purified.

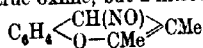
[With GOTTHARD TREBITZ.]—The condensation of acetophenone, or of dypnone, with propionic anhydride in the presence of sulpho-propionic acid leads to the formation of 4 : 6-diphenyl-2-ethylpyrylium sulphopropionate, small, yellow crystals, or thin reddish-yellow plates, m. p. 163°. The corresponding iodide forms blood-red needles, m. p. 236–237°. These pyrylium salts are converted by the action of sodium acetate solution, or of other weak alkalis, into an amorphous, brownish-red substance, which very readily resinifies, does not lose water when heated in a vacuum, and is apparently 4 : 6-diphenyl-2-ethylidenepyran.

[With HELENE NITZSCHE.]—4 : 6-Diphenyl-2-styrylpyrylium chloride, m. p. 115°, or with 2H<sub>2</sub>O, intensely red crystals, m. p. 105°, is obtained by warming 4 : 6-diphenyl-2-methylpyrylium chloride (+ 2H<sub>2</sub>O) and benzaldehyde at 100°. The iodide forms small, dark brownish-red needles, m. p. 183–184°. The action of dilute sodium hydroxide or sodium acetate solution on an aqueous solution of either of these salts gives an amorphous, flocculent, orange-red precipitate, which has m. p. 120°, and does not resinify on drying. It is apparently the pseudo-base, 4 : 6-diphenyl-2-styrylpyranol.

W. S. N.

**The Beckmann Conversion of Oximes into Amides.** ERNST BECKMANN and ERICH BARK (*J. pr. Chem.*, 1923, [ii], 105, 327–349).

—The oxime of 1 : 2-dimethylchromone (Petschek and Simonis, A., 1913, i, 890) is not a true oxime, but a nitroso-derivative,



(Simonis and Elias, A., 1916, i, 499), since it does not undergo the Beckmann transformation. It is, in fact, unaffected by treatment with phosphorus pentachloride, anhydrous hydrogen chloride, acetyl chloride, glacial acetic acid, or acetic anhydride; the action of concentrated sulphuric acid gives a sulphonic acid, C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>NS, m. p. 225°, silver salt, m. p. above 280°. The nitrogen cannot be removed from the oxime by boiling it with hydrochloric acid, sulphuric acid, sulphurous acid, sodium hydroxide solution, or formaldehyde solution; a semicarbazone or phenylhydrazone of dimethylchromone cannot be prepared.

The oxime of 1-thio-2 : 3-dimethylchromone (Simonis and Elias,

*oc. cit.*) is a true oxime, but passes into gummy products when an attempt is made to effect its transformation by means of the usual reagents.

Isatinoxime is unaffected by treatment with sulphuric acid, gaseous hydrogen chloride, acetyl chloride, or acetic anhydride. The use of a mixture of phosphoryl chloride and phosphorus pentachloride leads to the formation of *o*-cyanophenylcarbimide, which Borsche and Jacobs obtained (A., 1914, i, 322) by the use of phosphorus pentachloride alone. Under no conditions is a rearrangement with formation of a six-membered ring brought about. The action of benzenesulphonyl chloride on isatinoxime in cold or boiling pyridine solution gives a *sulphonic acid*,  $C_6H_4 < \begin{smallmatrix} C(NOH) \\ N(SO_3H) \end{smallmatrix} > CO$ , ivory-coloured leaflets, m. p. 130—131° (insoluble *mercuric* salt).

The latter is likewise produced in attempting to prepare isatin-dioxime by the action of the same reagents on its *N*-acetyl derivative; this is not affected by treatment with pyridine alone, or with piperidine, but is converted into isatinoxime by the use of potassium hydroxide. The action of aqueous sodium hydroxide and benzoyl chloride on acetylisatin-dioxime gives isatinoxime benzoate, whilst *o*-cyanophenylcarbimide is obtained by the use of a mixture of phosphoryl chloride and phosphorus pentachloride.

The conversion of benzophenoneoxime into benzanilide is accomplished by fusion with the following chlorides: potassium, magnesium, calcium, aluminium, zinc, ferrous, ferric, mercuric, antimonious, antimonic, and phosphoryl chlorides. Benzophenoneoxime is unaffected by fusion with sodium chloride; by the action of carbonyl chloride in ethereal solution, or of nitrosyl chloride in chloroform solution, it is converted into benzophenone. The presence or absence of atmospheric oxygen apparently makes no difference. Antimony pentachloride and the trichloride effect this transformation with remarkable ease, the former even in cold chloroform solution. Conversion of the oxime into the ketone is also brought about by fusion with calcium, zinc, ferric, mercuric, or antimonic oxides, aluminium hydroxide, copper bronze, or anhydrous zinc sulphate, but hydrated zinc sulphate has no action. Benzanilide is quite unaffected by fusion with mercuric oxide, or by treatment with carbonyl chloride in chloroform solution. W. S. N.

**Chemical Reactivity and Conjugation: the Reactivity of the 2-Methyl Group in 2:3-Dimethylchromone.** ISIDOR MORRIS HEILBRON, HARRY BARNES, and RICHARD ALAN MORTON (T., 1923, 123, 2559—2570).

**Styrylbenzopyrylium Salts. III. The  $\gamma$ -Styryl Derivatives of 7-Hydroxy-2-phenyl-4-methylbenzopyrylium Chloride.** JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (T., 1923, 123, 2521—2531).

**Thiochromanones and the Products of their Transformations.** F. KROLLPFEIFFER and H. SCHULTZE (*Ber.*, 1923, 56, [B], 1819—1824; cf. Krollpfeiffer and Schäfer, this vol., i, 343).—A

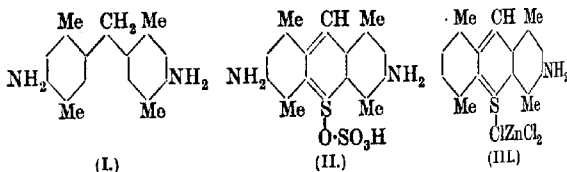
preliminary communication induced by the recent publication of Arndt (this vol., i, 826).

$\beta$ -Arylthiolpropionic acids are conveniently prepared by the action of an aqueous solution of sodium  $\beta$ -bromopropionate on the requisite mercaptan dissolved in 2*N*-sodium hydroxide solution.  $\beta$ -Phenylthiolpropionic acid,  $\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , colourless leaflets, m. p. 59°, b. p. 184°/10 mm.,  $\beta$ -*p*-tolylthiolpropionic acid, m. p. 70° (cf. Arndt, *loc. cit.*),  $\beta$ -*m*-xylylthiolpropionic acid, colourless leaflets, m. p. 84–85° after previous softening, b. p. 196–197°/12 mm.,  $\beta$ -1-naphthylthiolpropionic acid, m. p. 89–90°,  $\beta$ -2-naphthylthiolpropionic acid, m. p. 104–105°, b. p. 232°/12 mm., and  $\beta$ -2-tetrahydronaphthylthiolpropionic acid, m. p. 76°, after previous softening, b. p. 237°/12 mm., are described. Ring closure of the  $\beta$ -arylthiolpropionic acids to thiochromanones is readily effected by cold, concentrated sulphuric acid. Thiochromanone, colourless leaflets, m. p. 29–30°, b. p. 154°/12 mm. (*semicarbazone*, slender, colourless needles, m. p. 219–220°), 6-methylthiochromanone, colourless plates, m. p. 41–42°, b. p. 174°/10 mm. (*semicarbazone*, colourless leaflets, m. p. 235°, when rapidly heated), 6:8-dimethylthiochromanone,  $\text{C}_8\text{H}_2\text{Me}_2 < \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{S}-\text{CH}_3 \end{smallmatrix}$ , large, colourless plates, m. p.

38–39° (*semicarbazone*, colourless needles, m. p. 236–237°, when rapidly heated), 7:8-benzothiochromanone, coarse, yellowish-green prisms, m. p. 107°, and 5:6-benzothiochromanone, m. p. 68–69° (*semicarbazone*, m. p. 241–242°, when rapidly heated), are described.

Ring closure of  $\beta$ -2-tetrahydronaphthylthiolpropionic acid appears to yield a mixture of the two thiochromanones theoretically possible; the crude product of the reaction gives two *semicarbazones*, m. p. 255° and 224°, respectively, the former of which yields a *thiochromanone*, small, colourless platelets, m. p. 60–61°. H. W.

**Thiopyronines.** M. BATTEGAY and P. FRIES (*Bull. Soc. chim.*, 1923, [iv], 33, 1098–1103).—*p*-Xylidine does not behave in the normal manner with formaldehyde, but 2 mols. of the former condense with 1 mol. of the latter to give a substituted methane (I).



If this base be acetylated and dropped in small quantities with vigorous stirring into fuming sulphuric acid at 20°, condensation occurs, and the sulphate (II) of the substituted thiopyronine may be obtained, after removal of the acetyl groups, as small, green needles. This salt forms a *monodiaz*-derivative, indigo-blue in solution, and a *bisdiaz*-derivative, greenish-yellow in solution. On boiling the monodiaz-compound with alcohol and precipitating with zinc chloride, a salt of *apothio-pyronine* (III) is obtained. H. H.

**Selenopyrroles.** M. BATTEGAY and G. HUGEL (*Bull. Soc. chim.*, 1923, [iv], **33**, 1103—1106; cf. A., 1920, i, 629).—Two rules governing the formation of selenopyrroles are enunciated. First, the diphenylmethane used as parent substance must give a colour reaction with lead peroxide in acetic acid solution. Secondly, the substituents in the benzene nuclei must be such as will exert in fuming sulphuric acid solution a directing influence sufficient to cause the new substituent to enter in the ortho-position to the methane bridge. Examples are given to illustrate these rules and it is pointed out that the presence of nitro- or amino-groups is not in general conducive to successful condensation, although alkylation of the amino-group by removing its tendency to form an ammonium salt is distinctly advantageous.

H. H.

**Codeine and its Isomerides.** EDMUND SPEYER and WILHELM KRAUSS (*Annalen*, 1923, **432**, 233—265).—A simplification is described of Knorr's method (A., 1907, i, 151; 1908, i, 361) for separating the isomerides of codeine. *allo-ψ*-Codeine is obtained from its hydriodide by the action of ammonia as needles, m. p. 116—117°;  $[\alpha]_D^{25}$  —235.4°.

In accordance with Knorr's views (A., 1908, i, 42, 956) on the structure of codeine, *isocodeine*, *ψ-codeine*, and *allo-ψ-codeine*, the

latter behaves, when treated in dilute acetic acid solution with palladium black and hydrogen, like *ψ-codeine* (A., 1922, i, 47), giving *tetrahydroallo-ψ-codeine* (I), leaflets, m. p. 137—138°,  $[\alpha]_D^{25}$  —75.0°, in which the oxygen bridge is broken, since it gives a *diacetate*, small needles, m. p. 115°. It is evident that fission of the oxygen-carbon linking precedes the saturation of the bond 13—14, since *dihydro-ψ-codeine*, long needles, m. p. 128°

(*methiodide*, leaflets, decomp. 275°) is phenolic (soluble in alkali hydroxide solution); it is obtained by reducing *ψ-codeine*, either by means of sodium and alcohol, or electrolytically in 25% sulphuric acid solution, using lead electrodes. On further reduction by means of palladium-hydrogen, *dihydro-ψ-codeine* gives *tetrahydro-ψ-codeine*; the latter gives a *diacetate*, leaflets, m. p. 137—138°. *Dihydroisocodeine* (*loc. cit.*) gives a *monoacetate*, rods, m. p. 166°, *methiodide*, hexagonal tablets, m. p. 268—269°. The double compound, m. p. 147.5°, described by Lees (A., 1908, i, 42), consists of equal quantities of *isocodeine* and *allo-ψ-codeine*, since it gives equivalent quantities of *dihydroisocodeine* and *tetrahydroallo-ψ-codeine* when reduced in dilute acetic acid solution by means of palladium-hydrogen.

The *methiodide*, needles, m. p. 252°, of *tetrahydroallo-ψ-codeine* is converted by the action of hot, concentrated potassium hydroxide solution into *des-N-methyltetrahydroallo-ψ-codeine*, an oil, *hydriodide*, rectangular leaflets, m. p. 236°. This base forms an oily *methiodide*, from which an oily, nitrogen-free product is obtained by heating with 50% potassium hydroxide solution. The same behaviour is shown





pale yellow leaflets, m. p.  $180^{\circ}$ , are described) and pyrrolidine-dicarboxylamide. The ester is reduced by sodium and alcohol to *cis*-1-methyl-2:5-dihydroxymethylpyrrolidine, b. p.  $120-130^{\circ}/12$  mm. (the *hydrochloride*, *chloroaurate*, and *methiodide* are non-crystalline), but the yields are minimal by reason of the ready hydrolysis which occurs.

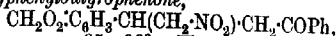
Ethyl *cis*-1-phenylpyrrolidine-2:5-dicarboxylate, b. p.  $205^{\circ}/13$  mm. (cf. Le Sueur, T., 1909, 95, 273), is readily obtained from the dibromo-ester and aniline. It is reduced by sodium and alcohol to *cis*-1-phenyl-2:5-dihydroxymethylpyrrolidine, a colourless, viscous liquid, b. p.  $200^{\circ}/11$  mm., which does not yield crystalline salts and is not converted by sulphuric acid into a homogeneous, dihydrated substance.

Ethyl *cis*-1-benzylpyrrolidine-2:5-dicarboxylate, b. p.  $205-207^{\circ}/12$  mm., yields a non-crystalline *picrate* and *methiodide*, a very hygroscopic *hydrochloride*, m. p.  $128^{\circ}$ , and a *chloroplatinate*, m. p.  $158^{\circ}$ . It is reduced by sodium and alcohol to *cis*-1-benzyl-2:5-dihydroxymethylpyrrolidine, a somewhat viscous, odourless liquid, b. p.  $210-211^{\circ}/13$  mm., which gives a non-crystalline *hydrochloride*, a *picrate*, m. p.  $139^{\circ}$ , and a *chloroplatinate*, m. p.  $177^{\circ}$ . The hydroxymethyl derivative is converted by sulphuric acid (70%) at  $175^{\circ}$  into 1-benzylmorphopyrrolidine, m. p.  $46^{\circ}$  (*hydrochloride*, m. p.  $255^{\circ}$ ; *chloroplatinate*, m. p.  $134^{\circ}$ ; *picrate*, m. p.  $164^{\circ}$ ; *methiodide*, m. p.  $249^{\circ}$ ). It is converted by cyanogen bromide into the *product*,  $C_{20}H_{24}ONBr$ , m. p.  $258^{\circ}$ , and a compound which appears to be essentially 1-cyanomorphopyrrolidine. H. W.

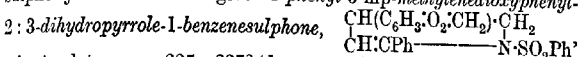
**The Catalytic Reduction of Nitro-compounds. II.  $\gamma$ -Nitroketones.** E. P. KOHLER and N. L. DRAKE (*J. Amer. Chem. Soc.*, 1923, 45, 2144-2150; cf. this vol., i, 666).—The reduction of three nitro-ketones, in which the nitro-radicle is in the  $\gamma$ -position to the carbonyl group, has been investigated, in the hope that ring formation between the carbonyl radicle and the partly reduced nitro-group might aid in elucidating the obscure mechanism of the reduction. Unfortunately, although cyclic compounds are formed, they are themselves so readily reduced that the process cannot be confined to a single step. Moreover, different products are formed by concurrent, as well as by consecutive reactions, and it is therefore impossible to deduce the course of the reaction.

*c*-Nitro- $\delta$ -phenylpentan- $\beta$ -one, lustrous needles, m. p.  $99-100^{\circ}$ , is prepared by the action of sodionitromethane on styryl methyl ketone in hot, methyl-alcoholic solution. It is reduced in methyl-alcoholic suspension, by means of platinum black and hydrogen, to 4-phenyl-2-methylpyrrolidine, a colourless liquid, b. p.  $112^{\circ}/10$  mm., which turns yellow when exposed to the air; it gives an *N*-benzoyl derivative, large prisms, m. p.  $82-83^{\circ}$ , and is converted by means of methyl sulphate and ice-cold 10% potassium hydroxide solution into 4-phenyl-1:2-dimethylpyrrolidine, isolated as its *hydrobromide*, slender, colourless needles, m. p.  $144-146^{\circ}$  (probably with decomp.). The condensation of piperonyl-

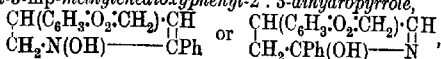
jdeneacetophenone with sodionitromethane gives  $\gamma$ -nitro- $\beta$ -mp-methylenedioxyphenylbutyrophenone,



slender needles, m. p. 95–96°. The reduction of this compound gives  $\gamma$ -amino- $\beta$ -mp-methylenedioxyphenylbutyrophenone, colourless needles, or plates, m. p. 129–130°, which becomes gummy and discoloured when kept moist or in solution, and gives a hydrochloride which cannot be purified. The amine reacts with benzenesulphonyl chloride to give 5-phenyl-3-mp-methylenedioxyphenyl-



minute plates, m. p. 225–227° (decomp.), after turning brown at 220°. Other products of the reduction are 2-phenyl-4-mp-methylenedioxyphenyltetrahydropyrrole, isolated as its hydrochloride, long, thin, white needles, m. p. about 208° (decomp.), and 1-hydroxy-5-phenyl-3-mp-methylenedioxyphenyl-2:3-dihydropyrrole,



colourless needles, m. p. 144–145°. The former is not produced by reduction of the dihydro-derivative, since the latter is present in the reduction mixture after all absorption of hydrogen has ceased. Moreover, the amino-ketone is stable in neutral, or weakly alkaline solution, and is therefore not the source of the pyrrole derivatives. The three products must consequently be formed by different paths. The reduction of  $\gamma$ -nitro- $\beta$ -phenylbutyrophenone gives an oily product which cannot be distilled, but from which the following compounds are isolated. The benzoate,  $\text{CHPh}\text{---}\text{CH}\text{>CPh}$  or  $\text{CHPh}\cdot\text{CH}_2\text{>CPh}\cdot\text{OBz}$ , colourless needles, m. p. 179–180°, of a hydroxydiphenyldihydropyrrole; 2:4-diphenyltetrahydropyrrole hydrochloride, thin, colourless needles, m. p. 171–172°, and the corresponding oxalate, a colourless solid. W. S. N.

**Synthesis of Methyl and Ethyl 1:2:3:5-Tetramethylpyrrole-4-carboxylate.** G. KORSCHUN and (MME) C. ROLL (*Bull. Soc. chim.*, 1923, [iv], 33, 1107–1108).—Methyl 1:2:3:5-tetramethylpyrrole-4-carboxylate is prepared by heating a mixture of methyl acetoacetate, methyl  $\alpha$ -chloroethyl ketone, and 33% aqueous methylamine in a sealed flask for several hours. The ester crystallises from petroleum, and melts at 101°. The ethyl ester is prepared by agitation of ethyl diacetylbutyrate with excess of 33% aqueous methylamine in the cold. H. H.

**Complex Salts of Sexavalent Osmium.** G. SCAGLIARINI and A. MASETTI ZANNINI (*Gazzetta*, 1923, 53, 504–507).—Compounds analogous to the oxyosmyl compounds (cf. Wintrebert, A., 1903, ii, 219) are not, so far as is known, formed by other metals of the platinum family, and the only salts which can be regarded as approaching them are the complex oxalates of tungsten and molybdenum,  $\text{WO}_3(\text{C}_2\text{O}_4)\text{K}_2\cdot\text{H}_2\text{O}$  and  $\text{MoO}_3(\text{C}_2\text{O}_4)\text{K}_2\cdot\text{H}_2\text{O}$  (cf. Rosenheim, 1893, i, 457). In view of the results obtained by Gibbs (A., 1882,

144), the authors have investigated the action of pyridine hydrochloride on potassium osmate. In strongly acid solution this action yields a compound,  $\text{OsO}_4\text{H}_2\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_2$ , which crystallises in yellowish-brown, fusiform needles, yields potassium osmate when treated with concentrated potassium hydroxide, and is probably pyridine trioxodichloro-osmonate,  $\left[ \begin{smallmatrix} \text{OsO}_4\text{Cl}_2 \\ \text{H}_2\text{O} \end{smallmatrix} \right] \text{H}_2\text{Py}_2$ . T. P. H.

**Complexes with Co-ordination Number Five.** A. SCHLEICHER, H. HENKEL, and L. SIES (J. pr. Chem., 1922, [ii], 105, 31–38).—The action of aniline on  $\text{trans-Pt}(\text{NH}_3)_2\text{I}_2$  gives a small quantity of  $\text{trans-Pt}(\text{NH}_3)_2(\text{NH}_2\text{Ph})_2\text{I}_2$ , together with an amorphous violet powder and a good yield of  $\text{trans-Pt}(\text{NH}_2\text{Ph})_2\text{I}_2$ . An attempt to prepare the latter from aniline and platinous iodide gave  $\text{cis-Pt}(\text{NH}_2\text{Ph})_2\text{I}_2$ , pale yellow crystals, which is also formed from aniline and  $\text{cis-Pt}(\text{NH}_3)_2\text{I}_2$ . The latter is obtained by the action of potassium iodide on the salt  $\text{cis-Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ , which is made by the action of silver nitrate on  $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ , an 80% yield of which is obtained, together with  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_2][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ , when ammonia reacts with potassium chloroplatinite. The *cis*- and *trans*-forms of the compound  $\text{Pt}(\text{NH}_2\text{Ph})_2\text{I}_2$  give, on treatment with pyridine, respectively, the *cis*- and *trans*-forms of the compound  $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{I}_2$ , in both of which the iodine atoms are ionisable. The action of concentrated hydrochloric acid on the *trans*-salt gives a mixture of yellow  $\text{trans-Pt}(\text{NH}_3)_2\text{I}_2$  and white  $\text{trans-Pt}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ , whilst the *cis*-salt gives solely  $\text{trans-Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ . *cis-Pt}(\text{NH}\_3)\_2\text{I}\_2 is easily soluble in aqueous ethylenediamine solution, whilst the *trans*-salt is soluble with difficulty. The product from the *cis*-salt is not the expected  $\text{cis-Pt}(\text{NH}_3)_2\text{en}]\text{I}_2$ , but the white compound,  $[\text{Pt en}_2]\text{I}_2$ , which is also formed from the *trans*-salt, or, together with  $\text{Pt en I}_2$  (glistening, yellow needles), by treatment of platinous iodide with aqueous ethylenediamine solution. The action of dilute sulphuric acid on an aqueous solution of the salt,  $[\text{Pt en}_2]\text{I}_2$ , causes separation of platinous iodide, with formation of a yellow solution from which a golden-coloured compound of unknown constitution is isolated. The action of chlorine on diethylenediamineplatinous chloride gives the yellow *monohydrate*, the white *dihydrate*, and the *trihydrate* of the compound  $\text{Pt en}_2\text{Cl}_4$ , from which, by the action of potassium chloroplatinate, a compound, probably  $[\text{Pt en}_2\text{Cl}_3][\text{PtCl}_4]$ , is produced. Two of the chlorine atoms in the compound  $\text{Pt en}_2\text{Cl}_4$  are evidently in the *trans* position with relation to the plane containing the ethylenediamine molecules, since they cannot be replaced by a further ethylenediamine molecule. Chlorination of the compound  $\text{Pt enCl}_2$  gives the compound,  $[\text{PtCl}_2\text{en}]\text{Cl}_2$ , yellow crystals, from which the isomeric *cis*-form of the compound,  $\text{Pt en}_2\text{Cl}_4$ , should be obtainable by boiling with ethylenediamine. The product is, however, triethylenediamineplatinic chloride. The action of cold pyridine on the compound  $[\text{Pt enCl}_4]\text{Cl}$  gives a salt,  $\text{Pt en}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$ , which is converted by means of ethylenediamine into dichloro-diethylenediamineplatinic chloride. Two of the chlorine atoms*

in the dipyridino-derivative are therefore considered to be in the *trans*-position with respect to the plane containing the ethylenediamine and pyridine molecules. The action of alcoholic bromine solution on an aqueous solution of diethylenediamineplatinous chloride gives a yellow compound,  $[\text{Pt en}_2\text{Br}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , which gradually turns green on exposure to the air, gives a white, caseous precipitate with silver nitrate, and a yellow salt with potassium chloroplatinate.

W. S. N.

**A New Method for the Preparation of Hydroxy-derivatives of Pyridine, Quinoline, and their Homologues.** A. E. TSCHITSCHIBABIN (*Ber.*, 1923, 56, [B], 1879—1885).—In analogy with the amination of the pyridine nucleus by means of sodamide (cf. Tschitschibabin and Zeide, A., 1915, i, 590), the hydroxylation can be effected with potassium hydroxide.

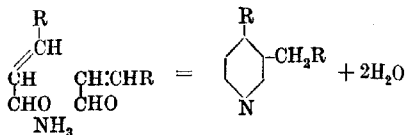
Quinoline reacts readily with potassium hydroxide at  $225^\circ$  with evolution of hydrogen and formation of the potassium derivative of 2-hydroxyquinoline; the success of the operation depends greatly on the care expended in the desiccation of the alkali and to some extent on its state of division. The yield of pure 2-hydroxyquinoline is not less than 80% of that theoretically possible. Small amounts of indole and, possibly, of 4-hydroxyquinoline, appear to be produced simultaneously. 2-Methylquinoline does not evolve hydrogen when treated with potassium hydroxide; it is, however, evolved from lepidine. The analogous reaction with sodium hydroxide can be observed only at temperatures above the boiling point of quinoline. Pyridine is attacked less readily by alkali hydroxides; it is, however, transformed by potassium hydroxide at  $320^\circ$  into 2-hydroxypyridine.

The course of the interaction between quinoline and barium oxide depends greatly on the content of the latter of barium hydroxide; it leads to the production of derivatives of indole and quinoline, but the change appears to be very complicated. H. W.

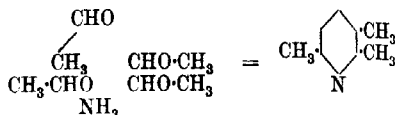
**The Synthesis of Pyridine Bases from Aldehydes and Ammonia.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 402—411).—The condensation of aldehydes with ammonia can follow several courses with the production of a variety of bases. One of the fundamental types is the condensation of three molecules of aldehyde with a molecule of ammonia previously studied in the case of acetaldehyde, butaldehyde, and valeraldehyde and leading to 2 : 3 : 5-trialkylpyridines (A., 1906, i, 451); this reaction is limited to saturated aldehydes of the general formula  $\text{CH}_3\text{R}\cdot\text{CHO}$ , whilst unsaturated aldehydes of the general formula  $\text{CHR}\cdot\text{CH}\cdot\text{CHO}$  follow the scheme given by Baeyer (*Annalen*, 1870, 155, 981) and by Dürkopff and Schlaugk (A., 1888, 607), in which only 2 mols. of aldehyde take part. The condensation of 3 mols. of a saturated aldehyde with 1 mol. of ammonia can, however, follow an alternative scheme (Tschitschibabin, *loc. cit.*) leading to 3 : 4 : 5-trialkylpyridines, and it is now pointed out that such a reaction actually does take place in some cases. Thus,  $\gamma$ -picoline is formed in addition to  $\alpha$ -picoline from acetaldehyde (see following abstracts)

r r\*

and ammonia and 2- and 4-phenylpyridines are produced in a similar way (Tschitschibabin, A., 1915, i, 638). It is now suggested that a fourth type of condensation, leading to 3-substituted pyridines, occurs to a limited extent and can be represented as the condensation of ammonia with two molecules of an unsaturated aldehyde (or four molecules of a corresponding saturated one), thus:



This reaction accounts for the isolation of 4-methyl-3-ethylpyridine from the reaction product of acetaldehyde and ammonia (following abstracts), whilst the formation of a new trimethylpyridine, which must be the 2:3:6-compound, is explained by the condensation of 4 mols. of acetaldehyde with ammonia, thus:



An alternative scheme is possible, but this would lead to the known 2:3:4-compound (Guareschi, A., 1900, i, 558). A scheme is also given by which 2- or 4-propylpyridines might be produced in the same reaction.

G. A. R. K.

**The Condensation of Aldehydes with Ammonia in the Presence of Alumina.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 411—413).—The reaction between aldehydes and ammonia takes place readily and with satisfactory yield on passing the gaseous mixture of the reacting substances over granular alumina at 200—350°; the optimum temperature depends on the aldehyde used. The apparatus used is similar to that commonly employed for the Sabatier reaction and is described in detail.

G. A. R. K.

**The Condensation of Acetaldehyde with Ammonia in the Presence of Alumina.** A. E. TSCHITSCHIBABIN, P. A. MOSCHKIN, and (MILE) L. S. TIASHELOVA (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 413—420).—The reaction was carried out using the method described in the preceding abstract, the temperature being maintained at about 300°. The crude mixture of tertiary bases was obtained in 60% yield and was subjected to fractionation, followed by fractional precipitation by means of picric acid; 60% of the mixture was finally separated in the form of pure compounds. Of these,  $\alpha$ - and  $\gamma$ -picoline constitute about 28% and 30%, respectively; 2-methyl-5-ethylpyridine 33%, and 4-methyl-3-ethylpyridine, about 6%. In addition to these bases, the highest boiling fraction contains two bases, one of which (b. p. 185.5—186.5°, *picrole*, m. p. 133°) is identical with the collidine obtained from acetylene

and ammonia in the presence of alumina (A., 1915, i, 638); the other forms a picrate crystallising in needles, m. p. 164–165°. The products of the reaction are thus essentially the same as those obtained from acetylene and ammonia and also from acetaldehyde and ammonia by the older method.

G. A. R. K.

**Products obtained on Heating Paracetaldehyde with Ammonia in Sealed Tubes.** A. E. TSCHITSCHIBABIN and (MLLE) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 420–427).—It is shown that the compounds produced under the conditions originally used by Dürkopf and Schlangk (A., 1888, 607) are essentially the same as those obtained from acetaldehyde and ammonia by the catalytic process (preceding abstract). By far the greatest percentage of the pyridine bases which were obtained in 30% yield consisted of 2-methyl-5-ethylpyridine, characterised by its picrate melting at 164.5°;  $\alpha$ -picoline was also isolated in quantity in addition to small amounts of  $\gamma$ -picoline and 4-methyl-3-ethylpyridine; a picrate melting at 139° and belonging to an unknown base (*chloroplatinate*, m. p. 190°) having the composition of a trimethylpyridine was also isolated. This picrate was not identical with that of Guareschi's 2:3:4-trimethylpyridine or the picrates obtained by Tschitschibabin (A., 1915, i, 638). Neither the trimethylpyridine prepared by Auerbach (A., 1893, i, 175) and by Knudsen (A., 1895, i, 562) nor any trace of lutidines could be found in the reaction product.

G. A. R. K.

**The Condensation of Propaldehyde with Ammonia.** A. E. TSCHITSCHIBABIN and (MLLE) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 428–446).—The condensation of propaldehyde with ammonia proceeds satisfactorily in the presence of alumina at 310–320°, the yield of tertiary bases being about 40%. These were subjected to separation through their picrates after a preliminary fractionation. The substances isolated consisted of the picrate of 3:5-dimethyl-2-ethylpyridine (parvoline) which constituted about 60% of the total, the picrate of 3:5-dimethylpyridine 18% and that of another parvoline, melting at 155–156° and crystallising in prisms. This parvoline appears to be identical with a compound obtained in addition to the first two by Dürkopf and Götsch (A., 1890, 794, 1002); it has b. p. 219–220° (corr.)/748 mm.,  $d_4^{20}$  0.9672,  $d_4^{25}$  0.9516,  $d_4^{27}$  0.9464,  $n_D$  1.5064, and gives a chloraurate, m. p. 138°. On oxidation the base yields a dibasic acid, m. p. 261°, identical with that obtained by Dürkopf (*loc. cit.*) which this author wrongly believed to be dimethylpyridinedicarboxylic acid and is now proved to be 4-ethylpyridine-3:5-dicarboxylic acid by its conversion into 4-ethylpyridine (picrate, m. p. 69°, *chloroplatinate*, m. p. 108°); the structure of this base is confirmed by its synthesis from pyridine and ethyl iodide. From these facts, it is concluded that the second parvoline obtained by Dürkopf and Götsch and in the present research must be 3:5-dimethyl-4-ethyl pyridine. The formation of the two parvolumes as well as of lutidine from propaldehyde and ammonia is in complete agreement with the authors' views (preceding abstracts)

as to the mechanism of such reactions. It is suggested that the formation of Schiff's paraconiine (*Annalen*, 1873, 166, 88) which does not fall into line with these views was due to the presence of acetaldehyde in the butaldehyde used and that the product itself was a mixture composed chiefly of 2-propylpyridine and *i*-coniine (2-propylpiperidine); such condensations of mixtures of aldehydes with ammonia have already been observed (Stöhr, A., 1891, 579; 1892, 628) and it has now been found that mixtures of acetaldehyde with acraldehyde or ethylal and ammonia yield, in the presence of alumina, considerable quantities of pyridine. The possible synthesis of pyridine bases in plant organisms is also discussed. G. A. R. K.

**The Spontaneous Decomposition of Cyanoacetyl Chloride.**

G. SCHROETER and CHR. SEIDLER (*J. pr. Chem.*, 1922, [ii], 105, 165—176).—The spontaneous decomposition of cyanoacetyl chloride, which proceeds with violence and evolution of much hydrogen chloride when distillation under reduced pressure is attempted, takes place gradually at the ordinary temperature, or, better, at 0°, very little hydrogen chloride being formed. Together with other substances, which are soluble in water but do not crystallise readily, the chief product of the reaction is 5-chloro-1:3-dihydroxynicotinonitrile, slender, colourless needles, which turn yellowish-brown at 187—190°, and decompose at a higher temperature; the disodium salt, with 6H<sub>2</sub>O, is described. The constitution of this nitrile follows from its reactions. Although a disodium salt is formed by the action of concentrated alkali hydroxide solution, towards dilute (*N*/10) solutions the compound behaves as a monobasic acid. The chlorine atom is very firmly held; the action of 20% aqueous sodium hydroxide solution at 170—180° is required to eliminate the chlorine atom, one nitrogen atom being simultaneously removed, giving 1:3:5-trihydroxypyridine or 1:3:5-trihydroxynicotinic acid. The action of concentrated sulphuric acid on the nitrile gives 5-chloro-1:3-dihydroxynicotinamide, decomp. 220°, which, like the nitrile, gives a deep red coloration with ferric chloride in alcoholic solution, and behaves as an acid towards dilute alkali solutions. The prolonged action of alkali hydroxides causes almost complete elimination of the chlorine. The nitrile may be methylated by means of methyl sulphate in sodium hydroxide solution, giving a monomethyl ether, colourless crystals, m. p. 250° (decomp.), which is a monobasic acid, and gives a red coloration with ferric chloride; it forms a white, crystalline sodium salt, which reacts in boiling xylene solution with methyl sulphate, with formation of 5-chloro-1:3-dimethoxynicotinonitrile, m. p. 239—240° (decomp.). The latter is neutral towards cold sodium hydroxide solution, and does not give a coloration with ferric chloride. The chlorine is displaced by the action of boiling sodium hydroxide solution, or of boiling methyl-alcoholic potassium methoxide solution; the product of the latter reaction is 1:3:5-trimethoxynicotinonitrile, m. p. 260—261° (decomp.). The cyano-group in this compound is not converted into the amido-group, even when the action of cold concentrated sulphuric acid is prolonged during twenty-four hours. W. S. N.

**Substituted Indole Derivatives.** I. REINHARD SEKA (*Ber.*, 1923, 56, [B], 2058—2062).—The application of the Gattermann and Hoesch syntheses to 2-methylindole is described.

3-Aldehydo-2-methylindole,  $C_6H_4 \begin{smallmatrix} C(CHO) \\ \text{NH} \end{smallmatrix} > CMe$ , m. p. 198—199°, is obtained in 87% yield by the action of dry hydrogen chloride on 2-methylindole and anhydrous hydrocyanic acid dissolved in ether. 3-Acetyl-2-methylindole, m. p. 195—196°, is prepared by the action of dry hydrogen chloride on an ethereal solution of 2-methylindole and acetonitrile and decomposition of the ketimine hydrochloride by hot water; the yield is 33% of that theoretically possible. Under similar conditions, 2-methylindole and benzonitrile give a well-crystallised *ketimine hydrochloride* which is decomposed by boiling water into 3-benzoyl-2-methylindole, colourless needles, m. p. 181—182° (yield about 75%). 3-Phenylacetyl-2-methylindole, prepared in about 80% yield from phenylacetonitrile and 2-methylindole, crystallises in pale yellow needles, m. p. 196—197°. Ethyl cyanoacetate and 2-methylindole yield (?) *ethyl 2-methylindyl-3-β-aminoacrylate*,  $NH \begin{smallmatrix} C_6H_4 \\ CMe \end{smallmatrix} > C(NH_2)CH \cdot CO_2Et$ , yellowish-green needles, m. p. 135°. H. W.

**N-Substituted Oxindoles and Isatins.** R. STOLLÉ [with R. BERGDOLL, M. LUTHER, A. AUERBAHN, and W. WACKER] (*J. pr. Chem.*, 1922, [ii], 105, 137—148).—A preliminary account of a lengthy research on the preparation and reactions of *N*-substituted oxindoles and isatins.

The reactivity of the methylene group in *N*-substituted oxindoles is evidenced by numerous reactions. Thus 1-ethyloxindole and 1-ethylisatin, or the 1-phenyl derivatives, condense in the presence of piperidine to give the 3-hydroxy-3:3'-dihydroisoidindotin derivative, which may be dehydrated to the isoidindotin derivative. The condensation of phenylisatin (1 mol.) and phenyloxindole (2 mols.) is effected by the use of sodium ethoxide. Ethyl- or phenyl-oxindole can be condensed with phthalic anhydride, or with nitrosodimethylaniline. The anil formed in the latter reaction can react with a further molecule of oxindole in boiling acetic acid solution, giving the isoidindotin derivative.

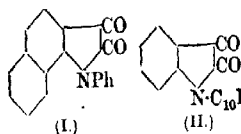
The isatins may be prepared from the oxindoles as follows. The action of ethyl nitrite in the presence of sodium ethoxide gives the isonitroso-derivative, which may then be hydrolysed, using mineral acids; or the 3:3-dihalogenated oxindole is prepared by means of hypochlorous or hypobromous acid, chlorine or bromine, or of phosphorus pentahalide, the dihalide being then hydrolysed to the isatin or isatinic acid (salt).

Hydrogen bromide in aqueous-alcoholic or carbon tetrachloride solution attacks the nucleus, giving, for example, 5-bromo-1-methyloxindole, 5:7-dibromo-1-methyloxindole, 5-bromo-1-ethyloxindole, or 5-bromo-1-phenyloxindole, the constitutions of which are proved by conversion into the isatin or isoidindotin derivatives. Hydrogen bromide in carbon tetrachloride solution acts on phenyloxindole, and moisture acts on the unstable additive compound of bromine

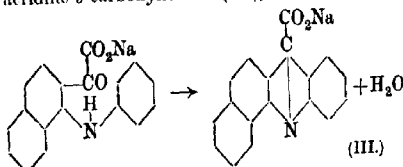
and phenyloxindole, to give 3:5-dibromo-1-phenyloxindole and 3:3:5-tribromo-1-phenyloxindole. The latter is also produced from 3:3-dibromo-1-phenyloxindole by the action of bromine in the presence of iron. 3-Bromo-1-phenyl-1-oxindole, which passes at 280° into diphenylisoidigotin, can only be prepared by warming molecular quantities of 3:3-dibromo-1-phenyloxindole and phenyloxindole in carbon tetrachloride solution. The additive product from bromine and ethyloxindole reacts with a further 2 mols. of bromine in carbon tetrachloride solution, giving 3:3:5-tribromo-1-ethyloxindole.

1-Methyloxindole is oxidised to dimethylisoidigotin by means of sodium hypoiodite. 1-Phenyloxindole undergoes hydrolytic fission when warmed with aqueous alkali hydroxide solution at 100°; the reverse change occurs when *o*-anilinophenylacetic acid is fused, or warmed in ethereal or alcoholic solution.

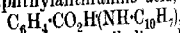
The action of oxalyl chloride on secondary anilines or naphthylamines gives oxamidyl chlorides, tetra-substituted oxamides occurring as by-products. Ring formation from oxamidyl chlorides frequently occurs in the absence of aluminium chloride, simply by heating, or even by warming in ethereal solution. Isatinic acids are oxidised to anthranilic acids by means of alkaline hydrogen peroxide. Most *N*-arylisatinic acids are converted by warming in alkaline solution into salts of acridinecarboxylic acid or its derivatives. Acridinecarboxylic acid is obtained in attempting to prepare phenylisatin by the action of oxalyl chloride on diphenylamine in the presence of aluminium chloride, the intermediate product being presumably *o*-anilinobenzoylformyl chloride. The action of oxalyl chloride on ditolylamine gives di-*p*-tolylamido-oxalyl chloride and 2:7-dimethylacridine hydrochloride; but sodium 5-methyl-1-*p*-tolylisatinate shows no tendency to pass into an acridine derivative.  $\alpha$ -Naphthyloxanilyl chloride,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NPh·CO·COCl, passes, on being heated alone or with aluminium chloride, into



1-Phenyl-6:7-benzoisatin (I), passes into the salt of 5:6-benzoacridine-9-carboxylic acid (III), when warmed in a strongly alkaline solution; the salt of the isatinic acid is formed immediately. The compound (III), as the free acid, loses carbon dioxide on being heated, giving the known 5:6-benzoacridine. Elimination of hydrogen chloride occurs when  $\beta$ -naphthyloxanilyl chloride is



1-phenyl-6:7-benzoisatin, m. p. 217°, (I), and 1- $\alpha$ -naphthylisatin, (II), m. p. 176°. The latter gives  $\alpha$ -naphthylanthranilic acid,



when oxidised in alkaline solution by means of hydrogen peroxide.

of the isatinic acid is formed immediately. The compound (III), as the free acid, loses carbon dioxide on being

heated alone, or in solution, with formation of 1-phenyl-4:5-benzoisatin (IV), which gives, on oxidation, 2-phenylaminonaphthalene-1-carboxylic acid. The compound (IV) passes, on treatment with an excess of alkali, into the salt of 7:8-benzo-acridine-9-carboxylic acid, from which the known 7:8-benzoacridine is obtained by elimination of carbon dioxide. 1-β-Naphthyl-4:5-benzoisatin is readily formed from di-β-naphthylamido-oxalyl chloride, even by the action of boiling water; it is converted on treatment with concentrated alkali into the salt of 1:2:7:8-dibenzoacridine-9-carboxylic acid, from which elimination of carbon dioxide gives 1:2:7:8-dibenzoacridine.

Phenylisatin is reduced by means of sodium hyposulphite to 1:1'-diphenylisatide,  $\text{NPh} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C(OH)} \cdot \text{C(OH)} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{CO} \end{smallmatrix} \text{NPh}$ , and 1-phenyldioxindole. The latter is coloured a deep indigo blue on addition of barium hydroxide solution to its pyridine solution; although dioxindole itself does not give any coloration (Hantzsch, A., 1921, i, 598).

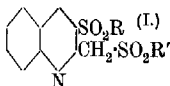
W. S. N.

**A New Illustrative Synthesis of Quinoline.** W. KÖNIG [with K. SEIFERT] (*Ber.*, 1923, 56, [B], 1853—1855).—Quinoline is produced when the substance  $\text{NPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{NPh} \cdot \text{HCl}$  is cautiously heated with fused zinc chloride. The observation confirms the theory, advanced by Beyer in 1886, that the primary product in Skraup's synthesis of quinoline is a substance of the type  $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CHO}$ , which passes successively into a dihydroquinoline and a quinoline derivative.

H. W.

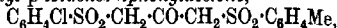
**Syntheses of 3-Arylsulphonyl-2-arylsulphonylmethylquinolines, and of 3-arylsulphonyl-2-phenylquinolines.** J. TRÖGER and K. VON SEELEN (*J. pr. Chem.*, 1923, [ii], 105, 208—231).—

The action of an excess of o-aminobenzaldehyde at 160° for two and a half hours on diphenylsulphonylacetone gives 3-benzenesulphonyl-2-benzenesulphonylmethylquinoline (I; R and R' = Ph), white needles, m. p. 168°, which is not a base, and is unaffected by fusion with potassium



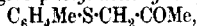
hydroxide. By the action of hot, concentrated hydrochloric acid under pressure, the α-Ph·SO<sub>2</sub>-radicle is replaced by hydrogen. 3-p-Toluenesulphonyl-2-p-toluenesulphonylmethylquinoline, yellowish-green, prismatic needles, m. p. 202°, is obtained by heating a mixture of o-aminobenzaldehyde and di-p-toluenesulphonylacetone at 155° for fifteen minutes. p-Chlorobenzenesulphonylacetone, white crystals, m. p. 83°, is formed by heating monochloroacetone and sodium p-chlorobenzenesulphinate in alcoholic solution at 100° for about an hour; its phenylhydrazone forms colourless, four-sided leaflets, m. p. 161°. The action of bromine (1 mol.) in glacial acetic acid solution on the sulphonylacetone gives ω-bromo-p-chlorobenzenesulphonylacetone, white, stellate clusters, m. p. 142°, which reacts with sodium p-chlorobenzene-

sulphinate in boiling alcoholic solution to give *di-p-chlorobenzene sulphonylacetone*, large, yellowish-white plates, m. p. 166°. When the latter is heated at 165° for fifteen minutes with *o*-aminobenzaldehyde, the product is *3-p-chlorobenzenesulphonyl-2-p-chlorobenzenesulphonylmethylquinoline*, yellow plates, m. p. 197°. *p*-Chlorobenzenesulphonyl-*p*-toluenesulphonylacetone,



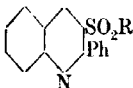
pale yellow needles, m. p. 163° (*oxime*, m. p. 214°), is prepared by heating equivalent quantities of sodium *p*-chlorobenzenesulphinate and  $\omega$ -bromo-*p*-toluenesulphonylacetone in alcoholic solution for about two hours. When this sulphonylacetone is heated for ten minutes at 165° with *o*-aminobenzaldehyde, it gives *3-p-chlorobenzenesulphonyl-2-p-toluenesulphonylmethylquinoline*, white plates, m. p. 199–200°. The constitution of this compound (cf. I) is proved by heating it with concentrated hydrochloric acid at 240° for a long time, whereby the  $-\text{SO}_2\cdot\text{R}'$  radicle is eliminated, giving *3-p-chlorobenzenesulphonyl-2-methylquinoline*. The interaction of sodium *p*-chlorobenzenesulphinate and  $\omega$ -bromobenzenesulphonylacetone in boiling alcoholic solution gives *benzenesulphonyl-p-chlorobenzenesulphonylacetone*, yellow needles, m. p. 129–130° [*semicarbazone*, yellow plates, m. p. 231° (decomp.)], which, when perfectly pure, reacts at 130–150° with *o*-aminobenzaldehyde during the course of about twenty minutes, to give *3-p-chlorobenzenesulphonyl-2-benzenesulphonylmethylquinoline*, greyish-white prisms, m. p. 157°. The constitution of the latter follows from the production of *3-p-chlorobenzenesulphonyl-2-methylquinoline*, by the action of concentrated hydrochloric acid at 240° for six to seven hours. *p*-Chlorobenzenesulphonyl-3-naphthalenesulphonylacetone,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Cl}$ , long, yellow needles, m. p. 167°, is produced by heating sodium  $\beta$ -naphthalenesulphinate and  $\omega$ -bromo-*p*-chlorobenzenesulphonylacetone for two to three hours in alcoholic solution; when heated for twenty minutes at 170° with *o*-aminobenzaldehyde, it gives *3-p-chlorobenzenesulphonyl-2- $\beta$ -naphthalenesulphonylmethylquinoline*, white clusters of needles, m. p. 163°, which is converted into *3-chlorobenzenesulphonyl-2-methylquinoline* by the action of concentrated hydrochloric acid at 240° for five hours.

*p*-Tolylmercaptan reacts with absolute alcoholic sodium ethoxide and chloroacetone to give *p*-tolyl acetonyl sulphide,



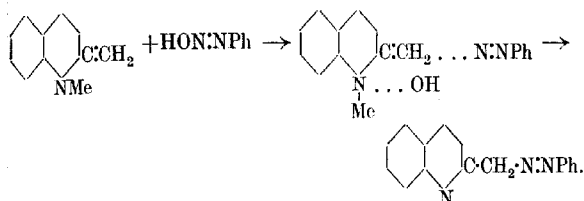
an oil, which gives a crystalline *sodium hydrogen sulphite* additive compound, and an oily *phenylhydrazone*. It has not been found possible in any way to prepare a quinoline derivative by condensing this acetone derivative with *o*-aminobenzaldehyde.

A series of 3-arylsulphonyl-2-phenylquinolines (formula annexed) is obtained by condensing *o*-aminobenzaldehyde with an arylsulphonylacetophenone, by heating at 200–240° for one and a half to two hours. *3-Benzenesulphonyl-2-phenylquinoline* forms pale yellow prisms, m. p. 208.5–209°, *hydrochloride*.



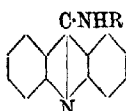
prisms, *nitrate*, *hydrogen sulphate*, *perchlorate*, white plates, *chloroplatinate*, yellow needles. 3-*p-Toluenesulphonyl-2-phenylquinoline* forms white plates, m. p. 243°, *perchlorate*, large, white plates, *nitrate*, clusters of small, white needles, *chloroplatinate*, orange needles. 3-*p-Chlorobenzene-sulphonyl-2-phenylquinoline* forms small, yellow needles, m. p. 237°, *nitrate*, white, hexagonal leaflets, *perchlorate*, slender, yellow needles, *chloroplatinate*, orange-red, flattened prisms, in clusters. W. S. N.

**The Anhydro-base of 2-Methylquinoline.** ALFRED ADAM (*Wissensch. Ind.*, 1923, 2, 2—8; from *Chem. Zentr.*, 1923, i, 1591—1592).—The methiodide of the anhydro-base of 2-methylquinoline reacts with diazotised aniline or *p*-nitroaniline in the presence of potassium hydroxide with formation of red or violet colouring matters. The reaction takes place with elimination of methyl alcohol, probably according to the following scheme :



The *p*-nitroaniline derivative shows halochromism with alkali hydroxides, changing from reddish-yellow to violet. The violet colouring matter is probably an inner complex salt formed by ring closure with the auxiliary valencies of nitrogen. The hydrazone and its hydrochloride also show halochromism. *Anilinodiazot-2-methylquinoline hydrochloride*,  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{Cl}$ , obtained by simultaneous addition of potassium hydroxide solution and diazotised aniline to an aqueous solution of 2-methylquinoline methiodide, forms reddish-yellow needles, m. p. 211—212°. An *acetyl* compound, corresponding with three molecules of acetic acid, forms ruby-red crystals, m. p. 202—203°. *p-Nitroanilinodiazot-2-methylquinoline hydrochloride*,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}_4\text{Cl}$ , forms dark red needles, m. p. 240—241°. The inner complex salt formed from the last compound by the action of potassium hydroxide forms dark violet needles, m. p. 171°. The same compounds are obtained when the ethiodide or amyl iodide is used in the place of the methiodide. *Quinoline-acrylic acid* is obtained as its *barium* salt, m. p. 197°, after discoloration at 165°, by the action of potassium carbonate on chloral-2-methylquinoline and subsequent addition of barium chloride. The *hydrochloride* forms needles, m. p. 184—185°. *2-Methylquinoline-p-nitrophenylhydrazone*,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4$ , forms yellowish-brown needles, m. p. 244—245°. The *hydrochloride*,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}_4\text{Cl}$ , red crystals, has m. p. 257—258°. G. W. R.

**Preparation of Derivatives of Acridine.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-PP. 360421, 364034, 364032, 367084, and Swiss Pat. 94950; from *Chem. Zentr.*, 1923, ii, 1249—1250).—9-Halogenacridines are treated with ammonia or primary aryl amines, or with secondary aliphatic amines in the presence of catalysts such as copper salts, or 5-alkoxyacridine or 5-aryloxyacridine derivatives are heated with ammonia, or primary or secondary



aliphatic amines. The compounds obtained are of the composition indicated by the annexed formula, where alkyl-, amino-, or alkoxy-groups may enter the acridine group. 5-Ethanolamino-3-ethoxyacridine is obtained by heating 5-chloro-3-ethoxyacridine (crystals, m. p. 144) with ethanolamine at 100°. It forms yellow crystals, m. p. 146°. 5-Chloro-3-ethoxyacridine is prepared by ethylation of 3-hydroxyacridone to 3-ethoxyacridone, m. p. 259—260°, and treatment of the latter compound with phosphorus pentachloride. 5-Chloro-3-ethoxyacridine and ethylamine give 5-ethylamino-3-ethoxyacridine, yellow crystals, m. p. 131—132°. 5-p-Hydroxyphenylethylamino-3-ethoxyacridine forms yellow crystals, m. p. 233°. The glycollate has m. p. 208°. 4-Aminoantipyrine and 5-chloro-3-ethoxyacridine give 5-antipyrilamino-3-ethoxyacridine, yellowish-red prisms, m. p. 257°. 5-Ethanolaminoacridine from 5-chloroacridine and ethanolamine forms long, yellow needles, m. p. 206°. 5-Aminoacridine forms yellow needles, m. p. 232°. 5-Diethyldiamino-3-ethoxyacridine is a thick oil; its hydrochloride forms red crystals, m. p. 177° after sintering. 5-Piperidino-3-ethoxyacridine is crystalline, m. p. 122°; the hydrochloride has m. p. 252°. 5-Ethoxyacridine is prepared by the action of sodium ethoxide on 5-chloroacridine; it has m. p. 83° and is easily changed by the action of mineral acids into acridone. With ethylamine it gives 5-ethylaminoacridine, crystals, m. p. 129°. 3:5-Diethoxyacridine obtained from 5-chloro-3-ethoxyacridine and sodium ethoxide forms needles, m. p. 83°. 5-Phenoxyacridine, from 5-chloroacridine and sodium phenoxide, has m. p. 112°. 5-Chloro-3-ethoxyacridine and sodium phenoxide give 5-phenoxy-3-ethoxyacridine, m. p. 85°, which with ammonia under pressure yields 5-amino-3-ethoxyacridine, m. p. 221°. Reduction of 5-chloro-2-nitro-8-ethoxyacridine gives 5-chloro-2-amino-8-ethoxyacridine, m. p. 192°, which with sodium ethoxide yields 2-amino-5:8-diethoxyacridine, and with sodium phenoxide, 2-amino-5-phenoxy-8-ethoxyacridine, m. p. about 100°. The three compounds last mentioned give with ammonia under pressure 2:5-diamino-8-ethoxyacridine, m. p. 124°. G. W. R.

**Preparation of Acridine Derivatives.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-PP. 364031, 364033, 364037; Swiss Pats. 93439, 93752, 93753, 94363, 94625, 94626, 94982, 96608, 96609; from *Chem. Zentr.*, 1923, ii, 1250—1251; cf. preceding abstract).—5-Hydrazinoacridine derivatives, nitro-5-aminoacridine derivatives, or nitro-5-hydrazinoacridine derivatives are submitted to reduction. For example, 5-phenylhydrazinoacridine, orange-yellow crystals, m. p. 173—174°, from phenylhydrazine and 9-chloro-

acridine, by reduction gives 5-aminoacridine, which can also be obtained by reduction of 5-hydrazinoacridine, orange needles, m. p. 289°, or of hydrazino-5:5-bisacridine,  $(C_{13}H_{18}N)_2 \cdot NH \cdot NH(C_{13}H_{18}N)$ , dark red crystals, m. p. 265°. Reduction of 5-phenylhydrazino-8-ethoxyacridine, a light yellow powder, m. p. 232–234°, yields 5-amino-8-ethoxyacridine. By nitration of 5-aminoacridine in the presence of strong sulphuric acid, dinitro-5-aminoacridine, red flakes, m. p. above 300° (decomp.), is formed. The sulphate gives by reduction a triaminoacridine which forms dark red leaflets; the hydrochloride forms long, yellow needles. From 2-chloro-4-nitrobenzoic acid and aniline, 5-nitrodiphenylamine-2-carboxylic acid is obtained which by elimination of water yields 2-nitroacridine. The latter, with phosphorus pentachloride, gives 5-chloro-2-nitroacridine, yellow leaflets, m. p. 214°, which with ethyl alcoholic ammonia yields 2-nitro-5-aminoacridine, m. p. above 300° (decomp.). By reduction of this compound, 2:5-diaminoacridine is obtained; it forms yellow needles, m. p. 146°; the hydrochloride forms yellow crystals. 5-Nitro-4'-ethoxydiphenylamine-2-carboxylic acid, from 2-chloro-4-nitrobenzoic acid and *p*-phenetidine, is crystalline and has m. p. 233–234°. By elimination of water and subsequent treatment with phosphorus pentachloride, it gives 5-chloro-2-nitro-8-ethoxyacridine, crystals, m. p. 186–187°, which with ammonia yields 2-nitro-5-amino-8-ethoxyacridine, crystals, m. p. 310°, with yellow and red modifications. By reduction of the last compound, 2:5-diamino-8-ethoxyacridine is obtained. 2-Nitro-5-phenylhydrazinoacridine forms dark red crystals; the hydrochloride is an orange-red powder which gives by reduction 2:5-diaminoacridine. 2-Nitro-5-phenylhydrazino-8-ethoxyacridine is a red mass from which 2:5-diamino-8-ethoxyacridine is obtained by reduction. The last compound is also obtainable by reduction of 2-amino-5-phenylhydrazino-8-ethoxyacridine. 2:5-Diamino-8-methoxyacridine forms yellow crystals, m. p. 240–242°. The hydrochloride, yellow needles, is obtained by reduction of 2-nitro-5-amino-8-methoxyacridine. The last compound is obtained from 3-nitro-4'-methoxydiphenylamine-6-carboxylic acid, red needles, m. p. 235°, by way of 5-chloro-2-nitro-8-methoxyacridine, yellow needles, m. p. 216–218°. 2-Nitro-5-phenylhydrazino-8-methoxyacridine is a red substance, m. p. above 300°; its hydrochloride is obtained by treatment of the corresponding chloro-derivative with phenylhydrazine. Reduction of 2-nitro-5-amino-8-isoamylorxyacridine, red needles, m. p. 272°, or of 2-nitro-5-phenylhydrazino-8-isoamylorxyacridine, red crystals, yields 2:5-diamino-8-isoamylorxyacridine, which forms yellow needles, m. p. 205–206°; the hydrochloride has m. p. above 300°.

G. W. R.

**Preparation of Acridine Derivatives.** FARBERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-PP. 364035, 364036; from *Chem. Zentr.*, 1923, ii, 1251–1252; cf. preceding abstracts).—Acridine-5-carboxylazides are decomposed with elimination of nitrogen, and the intermediate products obtained are hydrolysed, or acridine-5-carboxylamides are treated with hypohalogenites.

*Acridine-5-carboxylazide* is prepared by esterification of acridine-5-carboxylic acid, treatment of the ester with hydrazine, whereby *acridine-5-carboxylhydrazide*, m. p. 244°, is obtained, and treatment of the last compound with sodium nitrite in acetic acid solution. The azide, which decomposes at the ordinary temperature, on being heated with sulphuric acid gives *5-aminoacridine sulphate*, needles, from which the free base is obtained. By heating the azide with ethyl alcohol, *5-urethanoacridine*,  $C_{13}H_9N \cdot NH \cdot CO_2Et$ , is obtained: it forms needles, m. p. 188—194°, and on being heated with 2*N*. sulphuric acid gives *5-aminoacridine sulphate*. *Acridine-5-carboxylamide*, m. p. 260°, yields on treatment with potassium hypobromite *5-aminoacridine*. In the same way, *3-chloroacridine-5-carboxylamide*, m. p. 243°, yields with potassium hypobromite *3-chloro-5-aminoacridine*, m. p. 273—274°.

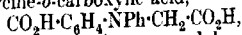
G. W. R.

**Preparation of Acridine Derivatives.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 176038; from *Chem. Zentr.*, 1923, ii, 1252; cf. preceding abstracts).—*3-Chloroacridine-5-carboxylic acid*, m. p. 264°, is prepared in the following way. *o*-Chlorobenzaldehyde, by treatment with magnesium ethyl iodide, gives *o*-chlorophenylethyl alcohol, which by oxidation with chromium trioxide yields *o*-chloroacetophenone, b. p. 98°/6 mm. By condensation of the last compound with *p*-chloroaniline, *3-chloro-5-methylacridine* is obtained, from which, by Kaufmann and Valette's reaction (A., 1912, i, 655), *3-chloro-5-aldehydoacridine*, m. p. 171—172°, is prepared. Oxidation of the last compound with chromium trioxide yields the carboxylic acid. *Ethyl 3-chloroacridine-5-carboxylate* has m. p. 71—72°. It gives with hydrazine the corresponding *hydrazide*, m. p. 210—211°, which by the action on it of sodium nitrite in acetic acid solution yields *3-chloroacridine-5-carboxylazide*. The last compound, on being heated with ethyl alcohol, gives *3-chloro-5-urethanoacridine*,  $C_{13}H_9NCl \cdot NH \cdot CO_2Et$ , m. p. 265°, from which by heating with dilute sulphuric acid *3-chloro-5-aminoacridine* is obtained.

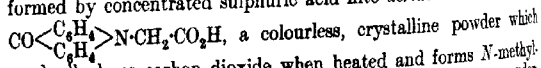
G. W. R.

#### **N-Diphenylglycine-*o*-carboxylic Acid and its Derivatives.**

MARTIN FREUND and ADOLF SCHWARZ (*Ber.*, 1923, 56, [B], 1828—1831).—Diphenylglycine-*o*-carboxylic acid,



m. p. 165—167°, is conveniently prepared by the interaction of potassium *o*-chlorobenzoate, potassium phenylaminoacetate, and potassium hydroxide in the presence of copper powder and water at 130—160°; the potassium salt is described. The acid is transformed by concentrated sulphuric acid into *acridone-10-acetic acid*,



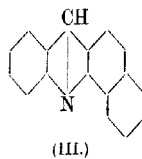
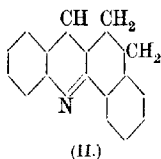
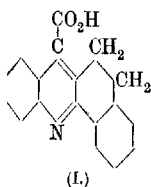
gradually loses carbon dioxide when heated and forms *N*-methylacridone. *Acridoneacetanilide*, a colourless, crystalline powder, and *methyl acridoneacetate*, yellow octahedra, m. p. 178—179°, are described. The presence of the ketonic group in *acridoneacetic acid* cannot be established by means of the customary reagents, since it does not react with hydroxylamine hydrochloride and with

phenylhydrazine yields the *phenylhydrazine* salt, m. p. 126°. Bromination of the acid in hot glacial acetic acid solution leads to the production of *dibromoacridoneacetic acid*, yellow octahedra, whereas nitric and sulphuric acids transform it into *dinitroacridoneacetic acid*, a yellow, crystalline powder, decomp. 169—170° (the sodium salt, red leaflets, is described).

Diphenylglycine-*o*-carboxylic acid is usually converted into indigotin by fusion with potassium hydroxide, but, under certain conditions, 1:1'-diphenylindigotin (cf. Friedländer and Kunz, A., 1922, i, 765) is obtained in small yield. H. W.

**Derivatives of Tetrahydrocarbazole. IV.** WILLIAM HENRY PERKIN, jun., and GEORGE CLIFFORD RILEY (T., 1923, 123, 2399—2408).

**Preparation of Polycyclic Derivatives of 2-Phenylquinoline-4-carboxylic Acid and Products Substituted in the Benzene Nucleus of the Quinoline Group.** TETRALIN G. M. B. H. (D.R.-P. 362539; from *Chem. Zentr.*, 1923, ii, 1248—1249).—1-Ketotetrahydronaphthalene or similar polycyclic ketones are condensed with isatin or its substitution products in alkaline solution. Isatin and 1-ketotetrahydronaphthalene give on heating at 100° in ethyl-alcoholic aqueous solution of potassium hydroxide and acidifying the products of reaction *dihydronaphthacridine-7-carboxylic acid* (I), needles, having m. p. 249°. On heating above the m. p. the last compound gives *dihydronaphthacridine* (II), with evolution of carbon dioxide. It is an almost colourless oil with b. p. 248—249°/12 mm. The *hydrochloride* has m. p. 228°, and the methiodide, m. p. 190°. By treating dihydronaphthacridinecarboxylic acid or dihydronaphthacridine with dehydrogenating reagents such as lead oxide,  $\alpha$ -naphthacridine (III), (cf. Ullmann and La Torre, A., 1904, i, 929), m. p. 108°, is obtained.



The isomeric *dihydronaphthacridinecarboxylic acid* obtained from 2-ketotetrahydronaphthalene and isatin is a colourless powder, n. p. 255°. 4-Keto-*s*-octahydroanthracene (Schroeter and Tetralin G. M. B. H., A., 1922, i, 1136), gives with isatin a light yellow, crystalline *carboxylic acid*, m. p. 210°. *p*-Bromodihydronaphthacridinecarboxylic acid forms crystals, m. p. 262° (decomp.). G. W. R.

**Phenylmethylisooxazolecarboxylic Acids.** MARIO BETTI and GIULIELMO SENSI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 615—618).—The solubilities in water of the two isomeric 5-phenyl-

3-methylisoxazole-4-carboxylic acids, m. p. 189° and 157° (A., 1922, i, 52), per 100 g. of water are, respectively, 0.0133 and 0.3739 g. at 13.5° and 0.0150 and 1.0890 g. at 35°. For the former acid the value of  $k$  is 0.02038; for the latter acid considerably higher values are obtained, but these diminish markedly as the dilution increases, probably owing to the ease with which the acid changes in aqueous solution. These results are in accord with the general rule that of two geometrical isomerides, that with the lower melting point is the more soluble and the more energetic.

T. H. P.

**Quinhydrone-like Compounds of 1 : 1'-Dialkylidihydro-4 : 4'-dipyridyls.** BRUNO EMMERT and VALENTIN DÖLLEIN (*Ber.*, 1923, 56, [B], 2068—2071).—A solution of dipyridyl diisoamyl iodide in water is treated with silver oxide and filtered. The filtrate, when heated in an atmosphere of hydrogen at 95°, gradually becomes intensely blue and deposits resinous matter. If the solution is now treated with hydriodic acid or with dipyridyl diisoamyl iodide the separation of tetraisoamylidipyridylviolet iodide is observed. This may be regarded as a simple ionic reaction if it is admitted that the solution contains tetraisoamylidipyridylviolet hydroxide. The formation of the latter can be explained by the hypothesis that a portion of the molecule of diisoamylidipyridylum hydroxide or of its pseudo-base becomes oxidised at the expense of other molecules. The quinonoid component of the dye is thus produced which combines with unchanged diisoamylidipyridylum hydroxide.

A similar series of experiments with dibenzylidipyridylum hydroxide is recorded; in this case the violet coloration is developed without warming. The products formed by the addition of hydriodic or hydrobromic acids of dipyridyl dibenzyl iodide or -bromide are identified as tetrabenzylidipyridylviolet iodide and -bromide. The solution therefore contains tetrabenzylidipyridylviolet hydroxide.

H. W.

**Complex Metallic Derivatives of Indigotin.** II. K. KUNS and O. GÜNTHER (*Ber.*, 1923, 56, [B], 2027—2034).—In continuation of previous work (this vol., i, 155), it is shown that the formation of complex metallic compounds of indigotin and its derivatives takes place without the evolution of hydrogen; the metal therefore is united in the molecule solely by residual valencies. The indigotin compounds appear to be closely related to the metallic compounds of chlorophyll described by Willstätter.

The sodium derivative of indigotin,  $C_{16}H_{10}O_2N_2Na$ , blackish-green, multi-sided crystals, is prepared by heating indigotin with metallic sodium at 140—150° in the presence of anhydrous xylene in an atmosphere free from oxygen. It is stable when dry and is not affected by oxygen or concentrated sodium hydroxide solution; it is decomposed by water, alcohol, or acids, with regeneration of indigotin and formation of small amounts of ill-defined resinous compounds. The protracted action of the alkali metals at 150° yields dimetallic derivatives, of which the di-potassium compound is described. Close analogy in appearance and properties is shown

by the mono-sodium derivative and the additive compounds of indigotin with sodium hydroxide and ethoxide; the likeness extends to the additive compounds with tin tetrachloride,  $C_{16}H_{10}O_2N_2 \cdot SnCl_4$ , small, blackish-green needles, and with magnesium phenyl bromide,  $C_{16}H_{10}O_2N_2 \cdot MgPhBr$ ; the so-called additive product of indigotin and sodium phenoxide is really the ethoxide derivative.

Indigotin reacts with zinc in the presence of boiling naphthalene without marked evolution of hydrogen. Under similar conditions, zinc carbonate yields the compound  $C_{32}H_{20}O_4N_4 \cdot ZnO$ .

"Thioindigo" yields the sodium derivative,  $C_{16}H_{10}O_2S_2 \cdot Na$ , almost black crystals, with some difficulty; the additive compound with sodium ethoxide,  $C_{16}H_{10}O_2S_2 \cdot 2NaOEt$ , is also described.

The action of the alkali metals on diphenylindigotin can be studied only in the case of potassium at  $0^\circ$ . The unstable mono-potassium derivative,  $C_{56}H_{36}O_4N_4 \cdot K$ , and the di-potassium compound,  $C_{56}H_{36}O_4N_4 \cdot K_2$ , were analysed. They are decomposed by water into diphenylindigotin and by-products from which *N*-phenylisatin and *N*-phenylantranilic acid can be isolated. When heated with zinc amalgam in the presence of boiling toluene, diphenylindigotin yields the compound  $C_{56}H_{36}O_4N_4 \cdot Zn$ , which is too unstable to permit its isolation in substance.

H. W.

**4 : 5-Diaminopyrimidines and their Conversion into Purines.** WILHELM TRAUBE [with FRIEDRICH SCHOTTLÄNDER, CARL GOSLICH, ROBERT PETER, FRANZ ANDREAS MEYER, HEINRICH SCHLÜTER, WILHELM STEINBACH, and KARL BREDDOW] (*Annalen*, 1923, **432**, 266—296).—4-Amino-2 : 6-dihydroxypyrimidine (A., 1900, i, 416), from which the 4 : 5-diamino-derivative is obtained (*loc. cit.*), is now prepared by the action of ethyl cyanoacetate on an equivalent quantity of carbamide in the presence of 1—2 equivalents of sodium ethoxide in boiling alcoholic solution. 4-Amino-5-carbamido-2 : 6-dihydroxypyrimidine, slender, white needles, is obtained by boiling the sulphate of the 4 : 5-diamino-compound with potassium cyanate in aqueous solution; it loses ammonia at  $230^\circ$ , with formation of uric acid. The action of phenylcarbimide on 4 : 5-diamino-2 : 6-dihydroxypyrimidine sulphate in the presence of sodium hydroxide solution at  $0^\circ$  leads to the formation of 4-amino-5-phenylcarbamido-2 : 6-dihydroxypyrimidine, colourless needles, which is converted by boiling with dilute hydrochloric acid into 9-phenyluric acid; the formation of the latter proves that it is the 5-amino-group which is attacked by the phenylcarbimide, since the loss of ammonia from the isomeric 5-amino-4-phenylcarbamido-derivative could give 7-phenyluric acid.

4-Amino-2 : 6-dihydroxy-3-methylpyrimidine is made by boiling ethylcarbamide, ethyl cyanoacetate, and sodium ethoxide in alcoholic solution, and is used (*loc. cit.*) in preparing 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine; the latter is converted by the action of boiling acetic anhydride into 4-amino-5-acetamido-2 : 6-dihydroxy-3-methylpyrimidine,  $+2H_2O$ , clusters of slender needles, the sodium salt of which passes at  $230$ — $240^\circ$ , with loss of water, to the sodium salt (slender needles) of 3 : 8-dimethylxanthine,

+H<sub>2</sub>O, slender needles. The conversion of 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine into 3-methyluric acid (A., 1901, i, 52) may be effected by the action of cyanic acid, giving a substituted carbamide, which passes at 240°, with loss of ammonia, into 3-methyluric acid. Similarly, by the use of phenylcarbimide, a carbamide derivative is produced, from which ammonia is eliminated by boiling with hydrochloric acid, giving 9-phenyl-3-methyluric acid (cf. Meyer, *Diss. Berlin*, 1903). The use of phenylthiocarbimide in boiling aqueous-alcoholic solution gives 4-amino-5-phenylthiocarbamido-2 : 6-dihydroxy-3-methylpyrimidine, +1½H<sub>2</sub>O, which is converted by boiling with 20% hydrochloric acid into 8-thio-9-phenyl-3-methyluric acid, microscopic leaflets. When the latter is treated in dilute hydrochloric acid (*d* 1.08) solution with sodium nitrite, 9-phenyl-3-methylxanthine, needles, is obtained. 4-Amino-5-oxalylamido-2 : 6-dihydroxy-3-methylpyrimidine, +H<sub>2</sub>O, clusters of long needles, is obtained by fusing diaminodihydroxymethylpyrimidine with an excess of oxalic acid at 160–170° in a vacuum; it forms a crystalline disodium salt, which passes at 250–260° into the disodium salt of 3-methylxanthine-8-carboxylic acid, +1½H<sub>2</sub>O, white leaflets, or clusters of needles, barium salt, needles. This acid rapidly loses carbon dioxide at 160° to give 3-methylxanthine. 4-Amino-5-cyanoacetamido-2 : 6-dihydroxy-3-methylpyrimidine, white, glistening, flexible needles, is obtained by fusing diaminodihydroxymethylpyrimidine with cyanoacetic acid at 120–130°. It is converted by the action of sodium hydroxide into 3-methylxanthine-8-acetic acid, +H<sub>2</sub>O, clusters of white needles, methyl ester, needles. If, instead of cyanoacetic acid, succinic acid is used, first at 150°, finally under reduced pressure at 160–170°, the product is 4-amino-5-succinylamido-2 : 6-dihydroxy-3-methylpyrimidine, needles, the crystalline disodium salt of which passes at 250–260° into the disodium salt of 3-methylxanthine-8-propionic acid, +H<sub>2</sub>O, methyl ester, long, flexible needles, amide, slender needles.

4 : 5-Diamino-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine (*loc. cit.*) may be conveniently obtained by boiling *s*-dimethylcarbamide, ethyl cyanoacetate, and sodium ethoxide, in alcoholic solution. It is converted by the action of boiling acetic anhydride into 1 : 3 : 8-trimethylxanthine, colourless, rhombic prisms. The action of molten cyanoacetic acid at 120–130° under reduced pressure on diaminodihydroxydimethylpyrimidine gives 4-amino-5-acetamido-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine, needles, which is converted by the action of hot sodium hydroxide solution into theophyllinacetic acid.

The action of boiling, glacial acetic acid on 2 : 4 : 5-triamino-6-hydroxypyrimidine gives the 5-acetyl derivative, +H<sub>2</sub>O, stellate clusters of colourless needles, the sodium salt of which passes at 220–240° into the sodium salt of 8-methylguanine, colourless prisms, hydrochloride, +H<sub>2</sub>O, colourless prisms, sulphate, elongated, colourless, octagonal tablets, nitrate, oval leaflets. 8-Ethylguanine, slender, colourless needles (hydrochloride, +H<sub>2</sub>O, prisms), is similarly prepared from 2 : 4-diamino-5-propionamido-6-hydroxypyrimidine. Tri-

4-aminohydroxypyrimidine reacts with fused succinic acid at 160–170° under reduced pressure to give 2:4-diamino-5-succinylamido-hydroxypyrimidine, yellow needles, from which, by heating the dium salt at 250–260°, guanine-8-propionic acid is obtained; the methyl ester hydrochloride forms colourless needles, and has a sweet taste.

4-Amino-6-hydroxy-3-methylpyrimidine,  $+2\text{H}_2\text{O}$ , glistening, white crystals (hydrochloride, small, transparent rods), is obtained by heating an alcoholic solution containing sodium ethoxide, ethyl benzoacetate, and acetamidine hydrochloride. It is converted by the action of nitrous acid into the 5-oximino-derivative, stellate clusters of large, blackish-green crystals (sodium salt, faintly violet needles, violet potassium salt), which is reduced in boiling aqueous suspension by means of ammonium sulphide, giving 4:5-diamino-6-hydroxy-2-methylpyrimidine,  $+ \text{H}_2\text{O}$ , stellate clusters of transparent prisms, sulphate, hydrochloride, rhombic tablets. The amine is converted by the action of boiling concentrated formic acid into 6-hydroxy-2-methylpurine (2-methylhypoxanthine), colourless needles, hydrochloride, slender, transparent prisms, sulphate, rods, sodium salt, long, white, lustrous, monoclinic needles. Methylhypoxanthine is converted by the action of aqueous alcoholic sodium hydroxide solution and methyl iodide into 6-hydroxy-2:7-trimethylpurine, which forms an additive compound,  $+3\text{H}_2\text{O}$ , with sodium iodide, from which it may be liberated by treating its solution with silver oxide.

The action of benzaldehyde on 4:5-diamino-2:6-dihydroxypyrimidine (sulphate) in hot, aqueous solution, gives 4-amino-benzylideneamino-2:6-dihydroxypyrimidine, felted needles, which reduced in aqueous suspension by the aid of sodium amalgam gives 4-amino-5-benzylamino-2:6-dihydroxypyrimidine, lozenge-shaped leaflets, m. p. 265°, sulphate,  $+ \text{H}_2\text{O}$ , prisms or leaflets. The benzylamino-derivative is converted by boiling with formic acid into its methyl derivative, a heavy, crystalline powder, which passes at 0° into 7-benzylxanthine, prisms, m. p. 295° (decomp.). The latter is converted by means of aqueous sodium hydroxide solution and methyl iodide at 100° into 7-benzyl-1-methylxanthine, m. p. 30°, whereas the use of methyl sulphate gives 7-benzyl-1:3-diethylxanthine (7-benzyltheophylline). 7-Benzyltheophylline is so obtained by the action of methyl sulphate and sodium hydroxide solution on 7-benzyl-3-methylxanthine, m. p. 273°. This is obtained by heating the formyl derivative, m. p. 252°, of 4-amino-5-benzylamino-2:6-dihydroxy-3-methylpyrimidine, leaflets, m. p. 226°, which is formed by the reduction of the 5-benzylideneamino-derivative (Raabe and Nithack, A., 1906, i, 214). W. S. N.

**Dioximes.** XII. G. PONZIO (*Gazzetta*, 1923, 53, 507–513).—The author's conclusion that the compound obtained by the action of nitrogen peroxide on  $\alpha$ -phenylglyoxime is the oxide of benzoyl anide oxime (this vol., i, 1019), and not phenylglyoxime peroxide as suggested by Scholl or phenylfuroxan as proposed by Wieland and Semper, is not in accord with the supposed isomerisation of

this compound by alkaline-earth hydroxides or carbonates into 4-hydroxy-3-phenylfuran,  $O \begin{smallmatrix} \text{N:CPh} \\ \text{N:C-OH} \end{smallmatrix}$

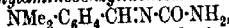
The author shows that the latter, although its existence has been recently confirmed by Wieland (A., 1921, i, 605), is merely the original oxide of benzoyl cyanide oxime in slightly impure condition.

When, however, this oxide is either heated with a little xylene or treated at the ordinary temperature in dilute benzene solution with phenylhydrazine, it undergoes isomerisation into 5-hydroxy-3-phenyl-1:3:4-oxadiazole (cf. Tiemann, A., 1885, 1216; Tiemann and Fock, A., 1886, 797; Falck, A., 1885, 1216; 1886, 797). The sodium salt of the latter,  $C_2ON_2Ph \cdot ONa$ , and the methyl ether, which crystallises in long, white needles, m. p.  $116^\circ$ , are described. The diazole is also obtained, together with  $\beta$ -anilino- $\alpha$ -phenylglyoxime when the oxide is treated in benzene solution with aniline.

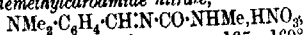
According to Wieland and Semper (A., 1908, i, 108), glyoxime peroxides, termed by them furoxans, do not react with Grignard's reagent. The author finds, however, that the oxide of benzoyl cyanide oxime reacts readily with magnesium methyl iodide, giving phenylmethylglyoxime.

T. H. P.

**A Reaction of Carbamide with *p*-Dimethylaminobenzaldehyde.** II. H. K. BARRENSCHEEN (*Biochem. Z.*, 1923, 140, 426-434).—In continuation of the author's work (A., 1922, ii, 794), definite derivatives of Ehrlich's aldehyde and carbamide have been prepared. *p*-Dimethylaminobenzylidenecarbamide,



yellow needles, m. p.  $188-190^\circ$ , is obtained by adding finely powdered *p*-dimethylaminobenzaldehyde to molten carbamide, but preferably by treating with ammonia the sulphate, lustrous, orange-red crystals of indefinite melting point, prepared by adding carbamide to the aldehyde dissolved in 5% aqueous sulphuric acid. The hydrochloride, orange-red, monoclinic needles, m. p.  $196-201^\circ$ , readily hydrolysed in aqueous solution, and *p*-dimethylaminobenzylidenemethylcarbamide nitrate,



rhombohedral, orange crystals, m. p.  $165-169^\circ$ , are also described. Phenyl-*p*-dimethylaminobenzylidenecarbamide hydrochloride,  $NMe_2 \cdot C_6H_4 \cdot CH:N \cdot CO \cdot NHPh, HCl$ , orange, monoclinic crystals, m. p.  $206^\circ$ , is obtained by passing dry hydrogen chloride into an ethyl-alcoholic solution of phenylcarbamide and the Ehrlich aldehyde. Similar coloured derivatives of thiocarbamide were obtained, but could not be isolated in a pure condition, owing to difficulties in recrystallisation. In an examination of the range of reaction of the Ehrlich aldehyde with substances containing an amino-group, it was found that formamide, acetamide,  $\alpha$ -bromodiethylcarbamide, and  $\alpha$ -bromo- and  $\alpha$ -iodoisovalerylcarbamide gave negative results. Positive reactions of varying intensity were given by biuret, allantoin, and ethylene- $\psi$ -carbamide, whilst parabanic and barbituric acids, the purines, guanidine, creatine, and creatinine gave no reaction. Of the amino-acids positive results were obtained only

in the cases of glycine, alanine, asparagine, glutamine, and glutamic acid. An attempt to make the reaction between carbamide and the aldehyde the basis of a colorimetric method of estimating the former proved unsuccessful.

J. P.

***p*-Nitrobenzeneazopyrogallol (Chrome Brown P.A.).** P. UILLARD (*Bull. Soc. chim.*, 1923, [iv], 33, 1084—1089).—An attempt to obtain a dye similar to alizarin, in that it will dye shades fast to washing and to light when mordanted with the sesquioxides of iron, aluminium, or chromium. For this purpose, a compound containing two adjacent hydroxyl groups and the chromophore  $-N=N-$  was selected. By coupling *p*-nitrodiazobenzene chloride with pyrogallol in the presence of sodium acetate, a mixture of isomeric *p*-nitrobenzeneazopyrogallols is obtained which may be separated by crystallisation from alcohol. The less soluble and more abundant fraction is thought to be the one in which coupling has taken place in the para-position to the 1- or 3-hydroxyl group of the pyrogallol, and gives an *acetyl* derivative, m. p. 193°. The dye, when chrome-mordanted, gives fast brown shades resembling alizarin. The other isomeride is thought to be the one coupled in the para-position to the 2-hydroxyl group. *Benzeneazopyrogallol*, chrome mordanted on wool, gives yellowish shades like alizarin.

H. H.

**Reduction of Nitronaphthalenes. I. Reduction of  $\alpha$ -Nitronaphthalene.** WILLIAM MURDOCH CUMMING and JAMES KING (J. Chem. Soc., 1923, 123, 2464—2470).

**Inner Azo-compounds from Azoles.** F. ARNDT and F. SCHENSCHER (*Ber.*, 1923, 56, [B], 1984—1988).—Triazoles and dithiazoles which according to their structure may be regarded as cyclic hydrazo-compounds should be capable of oxidation to the corresponding cyclic azo-derivatives. A review of the literature considered in conjunction with the author's own experiments shows that intensely coloured solutions are frequently produced from these substances. The conception of the products as azo-compounds must, however, be applied with caution and the simple azo-structure can only be assumed when the oxidised product is more readily soluble in ether and similar solvents than is the initial material and also does not exhibit abnormal acidity.

**Phenylguanethiosemicarbazide**,  $\text{NHPh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , colourless, crystalline granules, m. p. 146—148° (decomp.), is prepared by the action of thiosemicarbazide hydrochloride on phenyleyanamide in boiling aqueous solution; the *hydrochloride* sparingly soluble in water. It is converted by methyl sulphate in alkaline solution into the corresponding *S-methyl ether*, colourless, prismatic needles which soften at about 115°, and become converted to phenylguanazole. The ether is oxidised by potassium ferricyanide in dilute acetic acid solution to the corresponding azo-compound,  $\text{C}_6\text{H}_{11}\text{N}_5\text{S}$ , small, red needles, m. p. 110°, and is converted by boiling water into methyl mercaptan and phenylguanazole, colourless, prisms ( $+\text{H}_2\text{O}$ ), m. p. 226—228°, the *nitrate*,

m. p. 212° (decomp.), is described. The substance is not oxidised by potassium ferricyanide in an aqueous-alkaline medium, but is transformed by lead peroxide in dilute acetic acid solution in the presence of ether into 4-phenyldehydroguanazole,  $\begin{matrix} \text{N} \cdot \text{C}(\text{NH}) \\ | \\ \text{N} \cdot \text{C}(\text{NH}) \end{matrix} > \text{NPh}$ , pale brown platelets, m. p. 122—123°.

H. W.

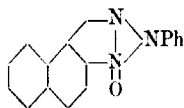
**Oxidation of *o*-Aminoazo-compounds in Acetic Acid Solution by Means of Hydrogen Peroxide.** G. CHARRIER and G. B. CRIPPA (*Gazzetta*, 1923, 53, 462—469).—With the view of obtaining better yields of *N*-arylbenz- and naphtha-1 : 2 : 3-triazoles,  $\text{Ar}'' < \begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix} > \text{NAr}'$ , than are given by the known methods, the authors

have investigated the action of hydrogen peroxide on solutions of certain *o*-aminoazo-compounds in glacial acetic acid. In some cases, the 1 : 2 : 3-triazoles are formed and in others aznitroso-derivatives, but the yields obtained are low and the difficulties of purifying the resultant products great. The results of Angeli and his collaborators (1906—1914) show that oxidation of azo-compounds by means of hydrogen peroxide yields the corresponding azoxy-derivatives which, when the molecule is unsymmetrical, may exist in two structurally isomeric forms. In the present case, it may be assumed that the *o*-aminoazo-compound is first converted into the two azoxyamino-compounds,  $\text{NH}_2 \cdot \text{Ar}'' \cdot \text{N} \cdot \text{NAr}' \cdot \text{O}$  and  $\text{NH}_2 \cdot \text{Ar}'' \cdot \text{NO} \cdot \text{NAr}'$ , in which, by further action of the peroxide, the amino- is transformed into the hydroxylamino-group. Elimination of a molecule of water from these hydroxylamino-derivatives by a reaction similar to that allowing of the passage from *o*-hydroxylaminoazoxybenzene to aznitrosobenzene (cf. Cusmano, A., 1921, i, 132) would then readily yield the corresponding triazole oxides,

$\text{Ar}'' < \begin{matrix} \text{N}=\text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix} > \text{NAr}'$ ; if, however, this mechanism resulted in the loss of the oxygen atom of the azoxy-group instead of that of the hydroxylamine radicle, a single aznitroso-derivative should be formed, as is actually found to be the case.

By a similar mechanism, it is easy to explain the formation of triazoles from the two isomeric *o*-aminoazoxy-derivatives, which are assumed to be the initial products of the action of hydrogen peroxide on the aminoazo-compounds. When the para-position of the radicle Ar is occupied, the triazole itself, and not the corresponding oxytriazole, is obtained; the cause of this is not yet ascertained.

The action of hydrogen peroxide on 1-benzeneazo-2-amino-naphthalene in acetic acid solution yields the first known representative of the aznitroso-derivatives of the naphthalene series, *N*-phenyl-naphthatriazole oxide, which, according to the above explanation of the mechanism of the reaction, has the annexed structure.



With potassium iodide in acetic acid solution, this compound

behaves similarly to its benzo-analogue, iodine being liberated and *N*-phenyl-1:2-naphthatriazole formed.

[With M. AGOSTONI].—Oxidation of 1-benzeneazo-2-aminobenzene by means of hydrogen peroxide in acetic acid solution gives *N*-phenyl-azinitrosobenzene, together with a compound, m. p. 158–159°, which is probably 2-amino-4'-hydroxyazobenzene,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  (cf. Cusmano, *loc. cit.*); the formation of the latter indicates that *o*-aminoazoxybenzene is the primary product in this reaction and that Wallach's transposition may occur, not only in concentrated sulphuric acid solution, but also in glacial acetic acid.

*N*-Phenyl-naphthatriazole oxide (see above) crystallises in colourless leaflets, m. p. 146°, and yields *N*-phenyl-1:2-naphthatriazole when reduced by means of zinc dust and acetic acid.

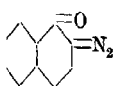
2-*p*-Tolyl- $\alpha\beta$ -naphthatriazole, m. p. 148–149°, prepared by the action of hydrogen peroxide on an acetic acid solution of 1-*p*-tolyl-azo- $\beta$ -naphthylamine, was previously obtained by heating the latter (cf. Charrier, A., 1910, i, 287). 2-*p*-Acetylphenyl- $\alpha\beta$ -naphthatriazole (Charrier, A., 1922, i, 771) is obtained from 1-*p*-acetylbenzeneazo- $\beta$ -naphthylamine.

1-*p*-Chlorobenzeneazo- $\beta$ -naphthylamine,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ , prepared from *p*-chlorophenyldiazonium chloride on  $\beta$ -naphthylamine, crystallises in slender, orange-red needles, m. p. 116°.

2-*p*-Chlorophenyl- $\alpha\beta$ -naphthatriazole,  $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\rangle\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ , prepared by treating the preceding compound in acetic acid solution with either chromic acid or hydrogen peroxide, forms slender, white needles, m. p. 186°. T. H. P.

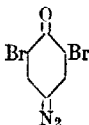
**Diazonium Salts of Anthraquinone (Anthraquinonediazonium Amalgam).** BATTEGAY and J. BÉHA (*Bull. Soc. chim.*, 1923, [iv], 33, 1089–1093; cf. this vol., i, 861).— $\alpha$ - and  $\beta$ -Anthraquinonediazonium chlorides were freed from hydrochloric acid and dissolved in distilled water. The solutions were then electrolysed in a cell maintained at 0° and fitted with a mercury cathode and a carbon anode. With a potential difference of 20 volts, gas was evolved and hydroxyanthraquinone formed, presumably by the loss of nitrogen from anthraquinonediazonium hydroxide. At higher voltages, particularly at 60 volts, the formation of a spongy mass on the surface of the cathode was observed. This is supposed to be anthraquinonediazonium amalgam, which decomposes to form mercury, nitrogen, and  $\alpha\alpha'$ -dianthraquinonyl. H. H.

**$\beta$ -Naphthaquinone- $\beta$ -diazide and Böhrer's  $\beta$ -Dibromonaphthaquinonediazides.** E. BAMBERGER, O. BÖCKING, and EMIL KRAUS (*J. pr. Chem.*, 1923, [ii], 105, 251–265).—A detailed account is given of the preparation of  $\beta$ -naphthaquinone- $\beta$ -diazide (annexed



formula), which has already been described under the name naphthalene-2:1-diazo-oxide (A., 1894, i, 295). This compound is converted by means of hydrogen chloride in ethereal solution into  $\alpha$ -naphthol- $\beta$ -diazonium chloride, yellow, glistening crystals, which readily loses hydrogen chloride when kept in a vacuum, or in

contact with water. The diazide is reduced by means of tin and fuming hydrochloric acid to  $\alpha$ -naphthol, and a greater quantity of  $\beta$ -amino- $\alpha$ -naphthol; the latter is reconverted into the diazide by the action of nitrous acid at  $0^\circ$ . The diazide reacts at  $70^\circ$  with phosphorus pentasulphide to give naphthalene- $\beta$ -diazosulphide, m. p.  $91-91.5^\circ$  (cf. Jacobson, A., 1894, i, 137). The action of a hot, concentrated, aqueous solution of potassium sulphite on the diazide gives potassium  $\alpha$ -naphthol- $\beta$ -diazosulphonate, glistening, orange-yellow crystals, which gives, with aqueous ferric chloride, a dark red coloration, and is reducible to  $\beta$ -amino- $\alpha$ -naphthol. The action of warm, dilute sulphuric acid on the diazide causes evolution of nitrogen, with formation of 1:4-naphthaquinol, and not the 1:2-derivative. The isomeric dibromo- $p$ -quinonediazides, decomp.  $137^\circ$  and  $145^\circ$ , respectively, described by Böhmer (A., 1882, 396), are identical. The compound, when pure, decomposes between  $145^\circ$  and  $154^\circ$ , according to the rate of heating. It has the annexed formula, since it is converted into  $s$ -tribromophenol, by the action of hydrobromic acid and copper.



W. S. N.

**$\beta$ -Naphthaquinone- $\alpha$ -diazide.** E. BAMBERGER, MARIE BAUM, and LEO SCHLEIN (*J. pr. Chem.*, 1923, [ii.] 105, 266—278).—If the action of nitrous acid on  $\alpha$ -amino- $\beta$ -naphthol (Grandmougin and Michel, A., 1892, 861) is conducted at  $0^\circ$ , the product contains, besides  $\beta$ -naphthaquinone,  $\beta$ -naphthaquinone- $\alpha$ -diazide, the preparation of which from  $\alpha$ -naphthylnitroamine (Bamberger, this vol., i, 28) is described in detail.  $\beta$ -Naphthaquinone- $\alpha$ -diazide is reduced by means of stannous chloride in concentrated hydrochloric acid solution to  $\alpha$ -amino- $\beta$ -naphthol.

Whereas  $\beta$ -naphthaquinone- $\beta$ -diazide gives 1:4-dihydroxy-naphthalene when warmed with dilute sulphuric acid (cf. preceding abstract), the  $\alpha$ -diazide is converted by means of the boiling acid into 1:2-naphthaquinol, together with small quantities of  $\beta$ -naphthol and  $\beta$ -dinaphthylidiquinol. 1:2-Naphthaquinol (1:2-dihydroxy-naphthalene) has m. p.  $102.5^\circ$ ; the low m. p., about  $60^\circ$ , recorded by Liebermann and Jacobson (A., 1882, 521) was due to the presence of dinaphthylidiquinol.

$\beta$ -Naphthaquinone- $\alpha$ -diazide reacts with phosphorus pentasulphide in warm benzene solution to give (cf. preceding abstract) 1:2-naphthalenediazosulphide, white needles, m. p.  $68.5^\circ$ .

When a solution of either the  $\alpha$ -diazide or the  $\beta$ -diazide in xylene is boiled for three to four hours, nitrogen is evolved, with the formation of bisnaphthaleneoxide,  $C_{10}H_6 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_{10}H_6$ , flat, glistening, white needles, m. p.  $256^\circ$ .

W. S. N.

**$\beta$ -Naphthaquinone- $\alpha$ -diazide and Methyl-alcoholic Potassium Hydroxide.** E. BAMBERGER and S. WILDI (*J. pr. Chem.*, 1923, [ii.] 105, 278—282; cf. preceding abstract).—The action of boiling methyl-alcoholic potassium hydroxide solution on  $\beta$ -naphthaquinone- $\alpha$ -diazide leads to the formation of  $\alpha$ -naphthol,  $\beta$ -di-

naphthol, and a methyl ether, columnar crystals, m. p. 90.5–91°, of 1:2-dihydroxynaphthalene. The action of boiling water on  $\beta$ -methoxynaphthalene- $\alpha$ -diazonium chloride gives  $\beta$ -methoxynaphthalene, and not the expected  $\alpha$ -hydroxy- $\beta$ -methoxynaphthalene, which would be identical or isomeric with the above methyl ether. The structure of the latter remains, therefore, undecided.

W. S. N.

#### Determination of the Hausmann Numbers of the Proteins.

JOHN KNAGGS (*Biochem. J.*, 1923, 17, 488–492).—When gelatin is left for some time in the presence of cold acid before being heated, higher diamino-acid figures are obtained than when the hydrolysis by boiling is proceeded with at once. This is due to partial hydrolysis of the protein in the cold and the formation of resistant polypeptides from the products of hydrolysis by polymerisation which are also precipitated by phosphotungstic acid. The fact has to be taken into consideration if a correct value for the percentage of diamino-nitrogen in the hydrolysis of gelatin is to be obtained, and the author has worked out the conditions it is necessary to observe in order to obtain correct results. Brucke's reagent, Mayer's reagent, cadmium iodide, and tannic acid do not precipitate diamino-acids from acid solution. Tannic acid is precipitated only in neutral solution and the precipitate thus obtained gives the same results as the phosphotungstic acid precipitate.

S. S. Z.

**The Catalytic Fission of Proteins according to Sadikov and Zelinski.** PERCY BRIEL (*Ber.*, 1923, 56, [B], 1887–1889).—In a recent communication (this vol., i, 867), Zelinski and Sadikov have obtained diketopiperazines in large amount by the hydrolysis of proteins with dilute hydrochloric acid (1–2%) at 180°, and have drawn the conclusion that the protein molecule is largely composed of diketopiperazine rings united by long methylene chains. This conclusion does not appear to be valid, since under the experimental conditions the simplest dipeptide, diglycine, gives a yield of at least 40% of diketopiperazine. It appears, therefore, that the hydrolysis in these circumstances is accompanied by polymerisation.

H. W.

#### Composition of the Specific Egg-albumin Precipitates.

FRITZ OTTENSOOSER (*Kolloid Z.*, 1923, 23, 176–178).—A number of experiments are described on the precipitate obtained when solutions of egg-albumin are mixed with the immune-serum of rabbits. They were undertaken with the object of confirming Jarisch's statement,  $\psi$ -globulin + lipoid substance  $\rightarrow$  euglobulin. The experiments show that freshly prepared precipitate from egg-albumin on warming at 55° passed completely and irreversibly into solution.

J. F. S.

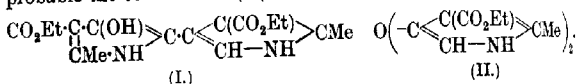
**Physico-chemical Investigations on Body-fluids. VII. The Change of Albumin into Globulin.** STEFAN RUSZNYÁK (*Biochem. Z.*, 1923, 140, 179–184).—The interconvertibility of serum-albumin and globulin under varying conditions, as shown by nephelometric measurements, is confirmed. Conditions favouring

the conversion of globulin into albumin are: heating at 42°, the addition of dilute alkalis. The reverse change is conditioned by: heating at from 42° to 60°, the addition of dilute acids, concentrated alkalis, alcohol, and a variety of other organic substances. Native serum-globulin is supposed to exist in part as a reversible, and in part as an irreversible modification which last cannot undergo conversion into albumin. J. P.

**The Oxygen Content of Methæmoglobin.** HERBERT ELDON ROAF and WILLIAM ARTHUR MERRETT SMART (*Biochem. J.*, 1923, 17, 579—585).—The addition of acid sufficient to convert oxyhæmoglobin into methæmoglobin liberates approximately half the amount of oxygen that would be given off by the same quantity of hæmoglobin when acted on by ferricyanide. S. S. Z.

**The Acid Nature of Oxyhæmoglobin.** ARCHIBALD VIVIAN HILL (*Biochem. J.*, 1923, 17, 544—546).—A theoretical contribution in support of Parsons' assertion that oxygenated blood is more acid than reduced blood. S. S. Z.

**Constitution of the Bile Pigments.** ERICH BENARY (*Z. physiol. Chem.*, 1923, 129, 304—306).—Fischer and Loy (this vol., i, 718) have expressed some doubt as to the constitution (I) assigned by Benary and Silbermann to the product,  $C_{15}H_{20}O_2N_2$ , of the condensation of ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate by means of concentrated hydrochloric acid and suggested as probable the constitution (II),



The author reaffirms the correctness of his view, pointing out especially that the reaction with ferric chloride indicates the presence of a hydroxyl group. W. O. K.

**Gelatin. II. The Methods of Purifying Gelatin.** JOHN KNAGGS, ALEXANDER BERNARD MANNING, and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1923, 17, 473—487).—It is practically impossible to free gelatin from its nitrogenous contaminants, produced mostly by thermal decomposition in the process of its preparation, by washing or dialysis. It is also difficult to free it entirely from electrolytes by washing with acid and water by Loeb's method. Gelatin thus purified can, however, be freed from almost the last traces of electrolytes by electrolysis, which procedure fails to remove substances of colloidal character, non-electrolytes, and weak electrolytes. It is possible to obtain a gelatin free from soluble nitrogenous contaminants by a process of "recrystallisation" in the following manner. When gelatin purified by washing and electrolysis is made up to a less than 2% aqueous solution it separates out as an insoluble hydrate. By repeated "recrystallisation" a supernatant fluid is obtained which contains about 10 mg. of the solute per 100 c.c. of the solvent,

a condition which indicates that the gelatin is free from soluble nitrogenous impurities. This concentration of the supernatant fluid remains constant independently of the strength of the solution from which the gelatin separates. Such a gelatin behaves almost as a pure substance in equilibrium with a saturated solution which contains 0.056% of gelatin.

S. S. Z.

**Effect of Time on the Physico-chemical Properties of Solutions of Gelatin.** R. DE IZAGUIRRE (*Anal. Fis. Quím.*, 1923, 21, 330—354).—The variation with time of the viscosity of gelatin solutions in the presence of increasing concentrations of hydrochloric acid shows a minimum corresponding with a maximum initial viscosity. This occurs at a concentration of 0.00912*N*. hydrochloric acid. Similar results were obtained for osmotic pressure. Gelatinisation is considered as consisting of a dehydration and not of the formation of a new chemical modification. Data are given for the mutarotation of gelatin solutions. The results are in accord with the formula  $[\alpha]_D = Kt^n$ .

G. W. R.

**The Action of Pepsin.** EMIL ABDERHALDEN and ANDOR FUDOR (*Fermentforsch.*, 1923, 7, 61—67).—Brief acid extraction of the mucous membrane of the pig's stomach gives a pepsin preparation which digests strongly, and also a strong biuret reaction, but not a protein reaction. It is not ultrafiltrable and there is no difference in activity when submitted to dialysis. Its action appears to be composite in nature, as under certain conditions of digestion there is a change of electrical conductivity and other properties, whilst under other conditions digestion proceeds without these changes.

H. K.

**The Action of Metals on Pepsin.** MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, 140, 149—153).—Pepsin is markedly inhibited by contact with powdered metallic copper and zinc, somewhat less by iron and cobalt, and not at all by nickel. Glycine does not protect the enzyme against copper or zinc.

J. P.

**Nephelometric Investigations on the Enzymatic Hydrolysis of Proteins.** P. RONA and H. KLEINMANN (*Biochem. Z.*, 1923, 140, 478—492).—The course of peptic hydrolysis of serum proteins dissolved in physiological salt solution was followed by means of the authors' nephelometric method. Curves plotted from the results show the initial rate of hydrolysis to be linear, but later the curve flattens out as the rate of hydrolysis diminishes. With increasing amounts of pepsin the linear portion of the curve is lessened relatively to the rest. The rate of hydrolysis is proportional to the ferment concentration. The results of varying the amounts of substrate while keeping the amount of enzyme constant revealed no simple proportionality.

J. P.

**Influence of Various Quinine Derivatives on the Fermentative Function of the Organism. II. The Influence of some Quinine and Urea Derivatives on Ptyalin.** I. A. SMORODNCEV and A. S. NOVIKOV (*Biochem. Z.*, 1923, 140, 12—16).—Quinine sulphate and hydrochloride accelerate the action of ptyalin on

starch. The dihydrochloride of quinine and carbamide, and carbamide and its salts inhibit the action of ptyalin, the salts of carbamide being much more active in this respect than is free carbamide. Thus the actions of these compounds noted in the case of trypsin (this vol., i, 412) are reversed in the case of ptyalin.  
J. P.

**The Secretion and Activity of Ptyalin.** HANS PRINGSHEIM and HARALD GORODISKI (*Biochem. Z.*, 1923, **140**, 175—178).—A comparison of the amylolytic activity of human saliva collected under carefully standardised normal conditions and after brushing the teeth with inactive paste and with paste containing different amounts of radioactive substance revealed no differences of a qualitative or quantitative nature.  
J. P.

**Asymmetric Hydrolysis of Racemic Amino-acid Esters by Esterase.** EMIL ABDERHALDEN, HANS SICKEL, and HARUJIRO UEDA (*Fermentforsch.*, 1923, **7**, 91—99).—*r*-Tyrosine ethyl ester was submitted to the action of pancreatic lipase in decinormal sodium hydrogen carbonate solution. There was preferential hydrolysis of the *l*-tyrosine ethyl ester with separation of *l*-tyrosine. The *d*-tyrosine ethyl ester was isolated from the mother-liquors by extraction with chloroform.  
H. K.

**The Action of Tyrosinase. Experiments with *d*-, *l*-, and *dl*-Tyrosine.** EMIL ABDERHALDEN and HANS SICKEL (*Fermentforsch.*, 1923, **7**, 85—90).—Tyrosinase from *Russula delica* added to equally concentrated solutions of *d*-, *l*-, and *dl*-tyrosine produced the red coloration first with *l*-tyrosine, then with *dl*-tyrosine and last with *d*-tyrosine. If examined polarimetrically, inactivation takes place before the development of the red colour and sooner with *l*-tyrosine than *d*-tyrosine. This inactivation occurs in absence of oxygen, but oxygenation of the three solutions after inactivation leads to simultaneous development of the red colour. The process of deamination therefore takes place at different rates in the three cases.  
H. K.

**The Tyrosinase-Tyrosine Reaction.** HENRY STANLEY RAPER and ARTHUR WORMALL (*Biochem. J.*, 1923, **17**, 454—469).—The velocity of the oxidation of tyrosine by tyrosinase is markedly influenced by the hydrogen-ion concentration of the medium. The limits of the reaction between which tyrosinase in potatoes acts are  $P_H$  5— $P_H$  10. The oxidation of tyrosine by the enzyme in buffered solution has a greater velocity at  $P_H$  8.0 than at  $P_H$  7.0; at the latter hydrogen-ion concentration the velocity is greater than at  $P_H$  6.0. The oxidation proceeds according to the formula of a unimolecular reaction. Tyrosinase produces from tyrosine at first a red substance, which is brought about by the action of the enzyme in the presence of oxygen. The red substance is then converted into a colourless substance. This conversion takes place spontaneously and more rapidly on warming. The colourless substance is eventually oxidised to form melanin. The last two processes take place in the absence of tyrosinase, but may be accelerated by it or by

other oxydases present in potato juice. In neutral and acid solutions the main product during the first six hours is the red substance, but in alkaline media the conversion of it into melanin proceeds so rapidly that solutions darken without any marked preliminary reddening. The authors show that tyrosinase does not contain a hydrolytic oxidation catalyst as suggested by Bach. Haehn's observations that tyrosinase inactivated by dialysis can be reactivated by the addition of certain salts has been confirmed. The acceleration of the enzyme by the addition of boiled potato juice is not due to inorganic constituents, but to some substance or substances present in the juice. This activator is not always present in boiled potato juice but is usually found in the boiled juice of new potatoes.

S. S. Z.

**Blood Catalase.** MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, 140, 63—112).—A comparative investigation of different methods of isolating blood catalase in solution. Corpuscles from horse-blood were centrifuged, washed with saline, dialysed against distilled water, and the resulting solution was evaporated. The dry powdered residue was dissolved in water to give a 1% solution, centrifuged, and filtered. This solution was then shaken for five minutes with one-fifth of its volume of chloroform, again centrifuged, and the supernatant light yellow solution separated from the chloroform and from precipitated proteins. This solution possessed from 70—80% of the catalase activity of the original dry powder and when fresh dog-corpuscles were used, without drying, the method gave an 80—90% extraction of catalase. Such purified solutions contain 2% of the nitrogen, and from 3 to 6% of the dry residue of the original watery solution before treatment with chloroform. They may be kept in an ice-box without change for several weeks. An alternative method of purifying the catalase is to adsorb it, together with hæmoglobin, from the centrifuged and filtered solution of the dry powder by means of tricalcium phosphate, and subsequently to wash it out with *M*/150-disodium hydrogen phosphate. Applied to the chloroform purified solution, this method results in a further elimination of nitrogen without corresponding loss of catalase activity. The optimum time of contact with the calcium phosphate is ten minutes, and for the washing out process fifteen minutes. The purified catalase solutions lost 20% of their activity after exposure for thirty minutes to a temperature of 45°, and were rendered inactive at 65°. Very dilute solutions of catalase, even in the presence of phosphate buffers, glycine or alanine, are unstable. Urea has a slight protective action.

J. P.

**A Heat-stable Catalyst in Animal Tissues which Destroys the Iminazole Ring and Unmasks Amino-groups.** WINIFRED MARY CLIFFORD (*Biochem. J.*, 1923, 17, 549—555).—The catalytic agent present in beef and cod which destroys carnosine in beef extract also destroys histidine in aqueous solution. Cod, washed beef, or liver added to histidine or muscle extract solutions at 100° decrease the colour obtained on diazotising the solutions which indicates a degradation of the iminazole ring. As the intensity of

the iminazole reaction falls there is a rise in amino-nitrogen which suggests a rupturing of the iminazole ring and a conversion of the ring nitrogen into amino-nitrogen.

S. S. Z.

**The Importance of Glycine and Potassium Cyanide for the Action of Urease.** TETSUGORA TAKAHATA (*Biochem. Z.*, 1923, 140, 154—157).—Urease in extreme dilution is rendered much more active by the addition of traces of potassium cyanide or glycine. The inactivation of urease by copper sulphate or mercuric chloride is inhibited by potassium cyanide and to a less extent, especially in the latter case, by glycine. Sodium cyanide acts like potassium cyanide, whilst potassium thiocyanate is very much less effective.

J. P.

**The Purification of Fumarase.** MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, 140, 161—165).—With the object of purifying the fumarase present in the dry powdered residue from a cold aqueous extract of human liver, the aqueous solution was treated with various precipitants. Methyl alcohol proved ineffective, but using various concentrations of ammonium sulphate, it was found that the enzyme was completely precipitated between 30% and 85% saturation. The aqueous solution prepared from this precipitate kept its activity for two weeks, but lost it on drying.

J. P.

**Sulphatase. I. The Enzymatic Hydrolysis of Phenyl Hydrogen Sulphate.** CARL NEUBERG and K. KURONO (*Biochem. Z.*, 1923, 140, 295—298).—An enzyme, to which the name *sulphatase* has been given, has been found in *Aspergillus oryzae*. Incubated at 37° with solutions of potassium phenyl sulphate, marked hydrolysis was obtained, amounting in sixteen days to 13.6% of the substrate.

J. P.

**Solubility of Insulin.** ERIK MATTEO PROCHET WIDMARK (*Biochem. J.*, 1923, 17, 668—670).—Insulin is insoluble or very slightly soluble in tetrachloromethane, ethyl acetate, ethyl alcohol, isobutyl alcohol, amyl alcohol, chloroform, acetone, light petroleum, ethyl ether, benzene, xylene, and pyridine. It is easily soluble in methyl alcohol, glacial acetic acid, phenol, and formamide. Several facts argue in favour of its being an albumose.

S. S. Z.

**Some Derivatives of Arsphenamine [Salvarsan].** WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, 45, 2182—2188).—It is shown that the relation between the mode of synthesis and the toxicity of salvarsan (this vol., i, 723) also holds for the production of salvarsan polyarsenide. The arsenic content of this substance varies between 41.87% and 50.81%; it is, in general, higher when the polyarsenide is produced by the reduction of *m*-amino-*p*-hydroxyphenylarsenious oxide and sodium arsenite by means of hypophosphorous acid (A., 1921, i, 370), than when *m*-nitro-*p*-hydroxyphenylarsinic acid and sodium arsenite are reduced by means of sodium hyposulphite. The toxicity of salvarsan polyarsenide is not very different from that of salvarsan itself.

In the preparation of sulpharsphenamine (this vol., i, 70) the

yield is improved by using 3 mols. of formaldehyde and 3 mols. of sodium hydrogen sulphite, instead of 2 mols. and 4 mols., respectively. It is unnecessary to use pure, freshly prepared sulphite, the commercial material being sufficiently pure. Also, it is unnecessary to start with salvarsan itself (i.e., the hydrochloride); the dry salvarsan base will do equally well. The toxicity of sulpharsphenamine is apparently not increased by using salvarsan, in the preparation of which the nitro-group has been improperly reduced (*loc. cit.*), or by the impurities present in the product.

When salvarsan polyarsenide is subjected to the procedure used in preparing sulpharsphenamine, a very soluble, orange-coloured sodium salt (deep red in solution) is produced, which is described as *sulpharsphenamine polyarsenide*. It is considerably more toxic than sulpharsphenamine, which is tolerated in doses of 400 mg./kg., not being tolerated in doses even as low as 200 mg./kg.

W. S. N.

**The Arsination of Phenol.** WALTER G. CHRISTIANSEN and ARTHUR J. NOBTON (*J. Amer. Chem. Soc.*, 1923, **45**, 2188—2192).—In the arsination of phenol by means of arsenic acid (Conant, A., 1919, i, 230; Jacobs and Heidelberger, A., 1919, i, 604), the yield of anhydrous sodium *p*-hydroxyphenylarsinate may be increased from 20% to 33% by vigorously agitating the reacting substances and allowing part of the water produced to distil off during the first stage of the reaction. It is suggested that a phenyl ester of arsenic acid may be an intermediate product in the formation of hydroxyphenylarsinic acids by this method. By distillation of aqueous solutions of *p*-hydroxyphenylarsinic acid, with steam, and estimation of phenol in the distillate, it is shown that hydrolysis to phenol and arsenic acid scarcely occurs at all at 100° (cf. Schmitz, A., 1914, i, 342).

W. S. N.

**As-Methyldihydroarsindole.** EUSTACE EBENEZER TURNER and FRANK WARD BURY (T., 1923, **123**, 2489—2492).

**Cyanurlyphosphinimines and the Pyrogenic Fission of the Methyl and Ethyl Esters of Normal Cyanuric Acid.** W. KESTING (*J. pr. Chem.*, 1923, [ii], **105**, 242—250).—*Ditriphenylphosphiniminecyanuryl azide*,  $\text{N}_3\text{C}\begin{smallmatrix} \text{N}^+\text{C}(\text{N}^+\text{PPh}_3) \\ \text{N}^+\text{C}(\text{N}^+\text{PPh}_3) \end{smallmatrix}\text{N}$ , a light

powder, m. p. 243° (decomp.), is formed by the interaction of triphenylphosphine and cyanuryl triazide in ethereal solution (cf. Staudinger and Meyer, A., 1920, i, 106); during the first stages of the reaction an intense green coloration is developed, which may be due to the intermediately formed phosphazide. This monoazide reacts with a further molecule of triphenylphosphine at 170—180° to give *cyanuryltri-triphenylphosphinimine*, a grey powder, m. p. 239°, which cannot be recrystallised because, apparently, it forms additive compounds with the solvents employed, e.g., benzene. When the vapour of ethyl cyanurate is passed, under reduced pressure, over a glowing platinum wire, it does not give

s s\*

ethyl cyanate, but ethylene and cyanic acid. Methyl cyanurate depolymerises with greater difficulty, giving methylcarbimide.

W. S. N.

**Organic Derivatives of Silicon. XXVII. A Probable Example of Tervalent Silicon.** FREDERIC STANLEY KIPPING (T., 1923, 123, 2598—2597).

**Organic Derivatives of Silicon. XXVIII. Octaphenyldiethylsilicotetranne.** FREDERIC STANLEY KIPPING (T., 1923, 123, 2598—2603).

**A New Phenyl Compound of Silver.** ERICH KRAUSE and BRUNO WENDT (*Ber.*, 1923, 56, [B], 2064—2066).—Freshly precipitated silver chloride is converted by an ethereal solution of magnesium phenyl bromide into a brown, granular powder, which readily decomposes when dry with sudden evolution of clouds of diphenyl fumes. It has not yet been possible to isolate the compound in a homogeneous state, but it appears that the ratio of silver to phenyl = 1:1. Similar compounds are obtained from magnesium *p*-xylyl bromide, magnesium  $\alpha$ -naphthyl bromide, and the magnesium compound of *p*-bromodiphenyl ether. The various colours exhibited by the solutions during the course of the reaction indicate that in each case a series of silver compounds is produced.

H. W.

### Physiological Chemistry.

**The Chemistry of Respiratory Tetany.** P. GYÖRGY and H. VOLLMER (*Biochem. Z.*, 1923, 140, 391—396).—During respiratory tetany following on forced breathing the blood-sugar diminished slightly whilst the blood salts showed no definite alteration. The urine showed a marked diminution in acidity and ammonia content, confirming the observations of other workers. It is concluded that the tetany is due to the increased alkalinity of the blood owing to elimination of carbon dioxide and does not depend on the action of any specific ion such as phosphate. J. P.

**The Diminution of the Blood-sugar in Normal Dogs by Ergotamine.** E. J. LESSER and K. ZIPF (*Biochem. Z.*, 1923, 140, 612—615).—Subcutaneous injection of from 5 to 10 mg. of ergotamine produces in dogs a lowering of blood-sugar of one hour to two hours' duration. In cases of human diabetes similar results were obtained in only one instance. The positive results are taken to indicate a sympathetic control of "sugar tonus." J. P.

**The Alkali Reserve of Blood-plasma in Avitaminosis.** J. A. COLLAZO (*Biochem. Z.*, 1923, 140, 254—257).—During the first six weeks of vitamin-free feeding, dogs showed no alteration in the alkali reserve of the blood-plasma, but later, especially during

the two weeks preceding death, a decrease was noted. In guinea pigs a marked decrease set in during the fourth week, but much less decisive results were obtained in the case of pigeons. The alkali reserve of dogs decreased during starvation from the third to the seventh day and subsequently rose slightly. It is concluded that the acidosis accompanying avitaminosis is not characteristic, but of secondary origin. J. P.

**The Alteration of the Sugar-content of Blood-serum in Vitro.** A. STASIAK (*Biochem. Z.*, 1923, 140, 420—425).—Blood-serum from normal and pathological cases kept in vitro at 37° for twenty-four hours shows a variable copper reducing value, in some cases increasing, in others decreasing. These alterations also occur in serum which has been kept for one hour at 56°, and are therefore not due to enzyme action. Endocrine extracts added to pure dextrose solutions under the same conditions produce no change. The changes are ascribed in the main to the colloids present in the serum, since similar variable copper reduction results were obtained with pure dextrose-globulin and dextrose-cholesterol solutions. Albumin and lecithin, on the other hand, gave negative results. J. P.

**Blood Clotting. VIII. The Prevention of Clotting by Neutral Salts.** BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1923, 140, 42—62).—The addition to blood of the sodium salts of cholic, glycocholic, taurocholic, and deoxycholic acids and of magnesium sulphate and sodium chloride prevents the alcohol or heat coagulation of the fibrinogen, and at the same time causes a marked and steady increase in internal friction as determined by the viscostagonometer. The mechanism of the prevention of clotting by these salts is the same as that postulated in the case of oxalated and citrated plasmas—the formation of a highly ionised fibrinogen-salt complex (*A.*, 1923, i, 410, 411). The case of sodium fluoride is different. It has no inhibiting action on fibrinogen-thrombin coagulation, nor does it prevent the alcohol precipitation of fibrinogen, and the washed and hæmolysed corpuscles from fluoride blood are effective coagulants, unlike those from oxalated or citrated blood. Here it is supposed that the corpuscles and not the fibrinogen itself are chiefly concerned. The fluoride so alters their permeability as to prevent the passage of the coagulating substance from corpuscles to plasma. Fibrinogen (fibrinisol) is regarded as a hydrophobe colloid and the whole question of coagulation is one of physico-chemical interaction between lyophile and lyophobic colloids. J. P.

**The Isolation of Soja-agglutinin and Anti-agglutinin.** KYOYETSURO FUJIWARA (*Biochem. Z.*, 1923, 140, 113—131).—Soja-agglutinin can be adsorbed by kaolin, aluminium hydroxide, and tricalcium phosphate from all of which it can be subsequently washed out by weak bases such as ammonia or disodium hydrogen phosphate. Weak acids are much less efficient in this respect. Use of excess of adsorbent renders the washing out more difficult.

The activity of soja-agglutinin is destroyed by boiling. Repeated injection of soja-bean extract produces in dog serum a specific anti-substance which inhibits the soja-agglutinin. This inhibition is not shown by normal serum. The anti-agglutinin can be adsorbed by the same substances as the agglutinin, but recovery by washing out is very imperfect. J. P.

**The Action of Metallic Copper on Ricin.** MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, 140, 140—148).—The agglutinating action of ricin on red blood-corpuscles is destroyed if the solution be treated with finely divided metallic copper and, in its stead, a hæmolytic action appears, irrespective of whether the ricin solution has been boiled, and so lost its agglutinating action, or otherwise. This hæmolytic action is attributed to the copper and not to any specific property of ricin. Glycine and potassium cyanide have no effect on the agglutinating action of ricin, but they inhibit the hæmolytic action of the copper-treated solution, without regenerating the agglutinating powers. Anti-ricin serum from dogs has no specific action on the hæmolysis produced by copper-treated ricin. The toxicity of ricin to mice is reduced by copper treatment. J. P.

**The Chemical Causes of Normal and Pathological Hæmolysis.** R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 470—479).—The hæmolytic constituents of normal human blood were extracted by means of boiling acetone or cold light petroleum, and showed the typical reactions of the higher fatty acids. Measurements of surface tension were made, which support the hypothesis that these acids are present in the blood in the form of their calcium salts. Finally, experimental pernicious anæmia was induced in rabbits by intramuscular or intravenous injection of linolenic acid. H. H.

**The Isolation of Croton and Anti-croton.** KYOYETSUO FUJIWARA (*Biochem. Z.*, 1923, 140, 132—139).—Croton-hæmolysin can be adsorbed from a 1% solution by means of kaolin, aluminium hydroxide, and tricalcium phosphate, but subsequent recovery by washing out is imperfect. Croton extract injected into dogs produces an anti-hæmolysin, absent from normal serum, which, like the hæmolysin, can be adsorbed but cannot be subsequently washed out from the adsorbents. J. P.

**The Influence of Cell Salts on Protein and Gaseous Metabolism and on Body-weight.** KAZUO ASADA (*Biochem. Z.*, 1923, 140, 326—347).—A dog kept in nitrogen equilibrium on a mixed diet of sufficient heat value and vitamin content, with sodium chloride as the only salt, was given a salt mixture containing calcium, magnesium, iron, potassium, chlorides, phosphates, and iodides. Increases were observed in oxidation, nitrogen retention, and in body-weight. The water excretion in urine and faeces was not definitely altered. The same results were produced by the addition of potassium chloride alone to the original diet. J. P.

**Intermediate Carbohydrate Metabolism in Avitaminosis.**

**I. Glycogen Formation and Exchange in Avitaminosis.** P. RUBINO and J. A. COLLAZO (*Biochem. Z.*, 1923, **140**, 258—267).—Administration of dextrose and other carbohydrates to avitaminosed pigeons, guinea pigs, and dogs results in a large and immediate increase in liver- and muscle-glycogen, followed by an equally rapid decline to sub-normal values. The maximum increase of blood-sugar occurs before the maximum rate of formation of glycogen. It is concluded that in avitaminosis the ability to form glycogen is unimpaired, and may even be increased, but that there is marked loss of the glycogen-storing powers. The rapid breakdown of glycogen does not produce an increase of blood-sugar, and is probably accompanied by the formation of toxic products. J. P.

**Polarimetric Observations on Solutions of Dextrose Subjected to Contact with Intestinal Mucosa of Rabbit.** DAVID STIVEN and EDWARD WAYMOUTH REID (*Biochem. J.*, 1923, **17**, 556—563).—The experiment of Hewitt and Pryde (A., 1920, i, 648) has been repeated thirty-four times. In eight cases, the solutions obtained from the gut had to be discarded as not clear enough for polarimetric estimations. In the remaining twenty-six experiments, no sign of mutarotation in the earlier minutes after removal of the solution from the gut was observed. S. S. Z.

**The Occurrence of Citric Acid in Sweat.** C. D. LEAKE (*Amer. J. Physiol.*, 1923, **63**, 540—544).—In twenty-four hours, 72.8 mg. of citric acid would be excreted in heat-sweat, or 60.7 mg. in work-sweat. Human saliva does not contain citric acid.

## CHEMICAL ABSTRACTS.

**The Hydrogen-ion Concentration, Carbon Dioxide Content, and the Ratio Ionic Calcium to Ionic Potassium, of the Cerebrospinal Fluid of Children.** JOACHIM BROCK (*Biochem. Z.*, 1923, **140**, 591—599).—The cerebrospinal fluids of various individuals ranging in age from nine months to ten years were examined with the view of obtaining normal data. The  $p_H$  determined by the indicator method was 7.50—7.55, and the carbon dioxide content 52 vol. %. Potassium and calcium were, respectively, 6.9 mg. % and 13.1 mg. %. The ratio of ionic calcium to ionic potassium of the cerebrospinal fluid is the same as that of the blood-serum. J. P.

**Colloid Chemistry of Protoplasm. I. General. II. The Electrical Charges of Protoplasm.** L. V. HEILBRUNN (*Amer. J. Physiol.*, 1923, **64**, 481—498).—Calcium or magnesium chloride tends to liquefy the protoplasm of sea-urchin eggs, whilst sodium, potassium, or ammonium chloride tends to increase its viscosity. The effects of these salts on the viscosity is thus in the reverse order of the adsorption of the kations by egg-albumin. It is consequently held that the colloids in the interior of the eggs are positively charged, a further increase in positive charge due to adsorption of kations causing decreased viscosity. The effects of various chlorides on the swelling of the vitellin membrane of sea-urchin eggs lead

the author to conclude that the exterior layer of protoplasm is negatively charged.

CHEMICAL ABSTRACTS.

**Does Adrenaline Affect the Metabolism of the Surviving Skeletal Muscles of the Frog?** F. R. GRIFFITH, jun. (*Amer. J. Physiol.*, 1923, 65, 15—29).—Adrenaline has no effect on the carbon dioxide production of surviving frog muscles. A modified Osterhout apparatus (*J. Gen. Physiol.*, 1918, 1, 17) used in the experiments is described.

CHEMICAL ABSTRACTS.

**The Behaviour of the Glycogen of the Frog in Anoxybiosis and Restitution.** IV. E. J. LESSER (*Biochem. Z.*, 1923, 140, 577—582).—The observations of Meyerhof (*Pflüger's Archiv*, 1920, 185, 20) on the disappearance of glycogen from, and the formation of lactic acid in, excised muscles cannot be extended to the whole animal, nor are his conclusions in agreement with those of the author. A series of investigations on summer and winter frogs is given, in which it is shown that, in the latter, during anoxybiosis, 40% of the total glycogen loss occurs in the liver, while, in the former, only 15% is so lost, in contrast to Meyerhof's findings. During restitution, the resynthesis of glycogen in the muscle is independent of the season, but during the winter it is in part masked by the concurrent diminution of liver glycogen.

J. P.

**The Significance of the Xanthidrol Reaction for the Microchemical Demonstration of Uric Acid in the Kidney.** K. WALTER (*Pflüger's Archiv*, 1923, 198, 267—278; from *Physiol. Abstr.*, 1923, 8, 272).—After injection of xanthidrol into rats, crystals of dixanthylurea are to be found in both glomeruli and convoluted tubules. This would suggest a process of secretion in both renal elements.

W. O. K.

**Blood-sugar Studies. III. Glycæmia and Glycosuria in Kidney Diseases and Effects of Peroral and Intravenous Administration of Sugar.** MAX ROSENBERG (*Arch. expt. Path. Pharm.*, 1923, 99, 143—161; cf. A., 1922, i, 482, 789).—In bad cases of renal insufficiency, the blood-sugar curve may not be normal, but may resemble that of diabetics, and there may be absence of glycosuria even although the blood-sugar is high. High blood pressure may be associated with a high fasting blood-sugar, but, if the kidney function is normal, with only a normal, or even sub-normal, rise after administration of dextrose.

W. O. K.

**The Behaviour of Amino-acids in the System Hide Powder-Tannin.** I. W. MOELLER (*Z. Leder. Gerberei Chem.*, 1923, 2, 212—227). The systems tannin-hide powder, formaldehyde-hide powder, basic chrome alum-hide powder have been studied with and without the addition of glycine. The amount of tannin, formaldehyde, and basic chrome alum adsorbed by the hide powder was diminished by the addition of glycine. The glycine and tanning material (tannin, formaldehyde, or basic chrome alum) resemble the system non-tannin-hydrolysed hide substance in their behaviour, and yield a substance which is not leather [cf. *J.S.C.I.*, 1923, 1083a].

D. W.

**The Theory of the Biochemical Degradation of Complex Structures.** O. STEFFUHN (*Fermentforsch.*, 1923, 7, 68—76).

—A comparison is made of the quantitative distribution of formic acid in the tissues of the rabbit and rat after injection of sodium formylglycine and after sodium formate. In all cases, the formic acid in the formylglycine was more easily destroyed by the tissues than by the free formate. The same results were found in experiments on ox-liver in vitro. H. K.

**Isolation and Determination of the Constitution of Tetramine, a Toxin from *Actinia equina*.** D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1923, 79, 113—120).—The toxin from *Actinia equina* was isolated by way of the picrate. It is shown to be tetramethylammonium hydroxide. G. W. R.

**Coagulation of Milk by Acid.** LEONARD ANDERSON (*Trans. Faraday Soc.*, 1923, 19, 106—111).—When hydrochloric acid is added to milk of various dilutions, the casein is precipitated to an extent which is greater the larger the amount of acid up to a maximum beyond which the casein redissolves to be again precipitated as chloride by further quantities of acid. The amount of acid required to effect each precipitation is inversely proportional to the dilution of the milk. The fat globules in the milk are carried down mechanically by the casein curd, and when this redissolves in excess of acid they rise to the surface, but remain for many hours without coalescing even in the presence of decinormal sodium hydroxide. Similar effects are observed in the cases of emulsions of benzene and olive oil in casein solution, so that it is probable that the protective agent for the fat globules in milk is a thin film of casein. The fat, benzene, or olive oil droplets may be caused to coalesce by removing the excess of protein by thorough washing with distilled water. A. R. P.

**The Action of Polished Metals on some Ferment Reactions of Milk and their Relation to Oligodynamic Phenomena.**

WALTER WEICHINGER (*Fermentforsch.*, 1923, 7, 110—133).—Contrary to Hildebrandt's observations, metals cannot reactivate the peroxidase of milk. Reductase is influenced in various ways by metallic ions, and this depends apparently on the degree of dissociation of the salt used. Catalase of milk is uninfluenced by metals. The typical oligodynamic inhibition of diastase by copper is also not observed in milk. H. K.

**New Picric Acid Compounds (Uropicrates).** P. BERGELL (*Z. klin. Med.*, 1922, 95, 63; from *Physiol. Abstr.*, 1923, 8, 274).—A crystalline precipitate produced from urine one-fifth saturated with sodium chloride and treated with Esbach's solution, yields pure uric acid when decomposed by alcoholic hydrochloric acid. The precipitate is almost wholly composed of picric acid and uric acid in equal proportions. W. O. K.

**Analysis of Liquid from a Paraovarian Cyst.** MARCEL GUERBET (*J. Pharm. Chim.*, 1923, [vii], 28, 177—178).—The liquid

had  $d^{20}_D$  1.005, was alkaline in reaction, and furnished no deposit when kept. Pseudomucin, globulin, urea, and fatty matter were present, together with sodium chloride and traces of sulphates and carbonates. The total solid content per litre was 10.3 g., 8.1 g. of this representing ash. Phosphates were absent. H. J. E.

**The Intermediate Fate of Chloral Hydrate in the Organism.** MUNEJI AKAMATSU and FERD. WASMUTH (*Arch. expt. Path. Pharm.*, 1923, **99**, 108—116).—If chloral hydrate or trichloroethyl alcohol is administered to guinea pigs, about one-half of the amount given is excreted as urochlorallic acid. As urochlorallic acid reduces copper there is an increase in the reducing power of the blood after administration of chloral hydrate. W. O. K.

**The Fate of some Halogen Derivatives of Benzene and of Benzene in the Animal Body.** T. S. HELE and E. H. CALLOW (*J. Physiol.*, 1923, **57**, xliii; from *Physiol. Abstr.*, 1923, **8**, 301).—One mol. of monochlorobenzene administered to dogs corresponds with one atom of sulphur in combination as sulphate (chlorophenyl sulphate) or as mercapturic acid (chlorophenyleystine) in the urine. The sulphur calculated from the output of halogen in organic combination corresponds with the excess of sulphur (etheral and neutral) over the normal average. The same holds good for *o*-dichlorobenzene, *m*-dichlorobenzene, and *p*-bromoanisole. The administration of benzene, *o*- or *m*-dichlorobenzene, but not of *p*-bromoanisole increases the neutral sulphur (mercapturic acid) in the urine. W. O. K.

**The Etheral Sulphate and Mercapturic Acid Syntheses in the Dog.** T. S. HELE (*J. Physiol.*, 1923, **57**, xlv-xlvii; from *Physiol. Abstr.*, 1923, **8**, 301).—It is doubtful whether phenol will combine with sulphate directly in the animal to form etheral sulphate, but after large doses of the non-toxic guaiacol and sulphate by the mouth, 60—80% of the administered sulphate was excreted as etheral sulphate. Likewise chlorobenzene, after oxidation to chlorophenol, will unite with sulphate to form etheral sulphate, as well as with cystine to form mercapturic acid. The rise in neutral sulphur was always about double that in etheral sulphur. It was found very difficult to upset this quantitative relation by the simultaneous administration of sodium sulphate or of cystine by the mouth. W. O. K.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Bacterial Reduction of Organically Combined Phosphoric Acid.** H. K. BARRENSCHEEN and H. A. BECKH-WIDMANNSTETTER (*Biochem. Z.*, 1923, **140**, 279—283).—Ox-blood inoculated with putrefying blood and kept under anaërobic conditions at 37° gives a positive Blondiot-Dusart reaction (evolution of phosphine in the

presence of nascent hydrogen), from which it is concluded that reduction of the organically combined phosphoric acid has occurred.

J. P.

**Detection of Phenols Produced by Bacteria.** WILLIAM H. BELL (*J. Infectious Diseases*, 1921, 29, 424—428).—The acidified medium is distilled with steam, and the distillate is treated with diazotised *p*-nitroaniline in alkaline solution; a yellowish-red colour is developed with concentrations of phenol as small as 1 in 500,000.

CHEMICAL ABSTRACTS.

**Urease as a Product of *Bacterium radicola*.** M. W. BEJERINCK (*Nature*, 1923, 112, 439; cf. Werner, this vol., i, 1046).—Urease is produced more profusely by pure cultures of *Bacterium radicola* than by the nodules, particularly by *Vicia*, *Trifolii*, and *Pisi* forms. Urease is also, in certain cases, a product of normal papilionaceous plants. Its existence is best demonstrated by a modification of the author's plate-method (*Centr. Bakt.*, 1893, II, 5, 323).

A. A. E.

**Preparation of a Urease Solution from Bacteria.** TETSUOORA TAKAHATA (*Biochem. Z.*, 1923, 140, 168—170).—From dried cultures of *Bacillus proteus* a soluble urease has been extracted by the use of various phosphate solutions.

J. P.

**Bacterial Catalase. IV.** J. HAGIHARA (*Biochem. Z.*, 1923, 140, 171—174).—By precipitating cultures of *Bacillus proteus* with methyl alcohol and by subsequently extracting the precipitate with water, purified catalase preparations were obtained with from 60 to 80% of the original activity of the culture. The purified solutions, unlike the original cultures, contain only traces of amino- and ammonia nitrogen.

J. P.

**The Fermentation of Arabinose and Xylose by certain Aërobic Bacteria.** E. B. FRED, W. H. PETERSON, and J. A. ANDERSON (*J. Bact.*, 1923, 8, 277—286).—The fermentation of pentoses by *Bacillus vulgaris*, *Acetobacter sorbose*, *A. xylinum*, *B. herbicola aureum*, and two yellow coccus forms called A and B are studied. The rates of fermentation of xylose and in certain cases of arabinose were slower than with the facultative anaërobic bacteria. The products of fermentation of the pentoses depend on the kind of organism. The ratio of the products depends on the age of the culture. *B. vulgaris* ferments xylose with the formation of acetone, ethyl alcohol, carbon dioxide, and a small amount of fixed acids. As the culture grows older the ratio of acetone and ethyl alcohol to carbon dioxide decreases. The maximum amount of acetone and ethyl alcohol is found about the sixth day. In the case of *A. xylinum*, an increase in the age of the culture is accompanied by an increase of acetone and ethyl alcohol. Although in different proportions, the substances obtained by the breaking down of xylose are the same as those noted with *B. vulgaris*. The remaining organisms studied ferment the pentoses slowly. They form a trace of acid, but the chief end-product is carbon dioxide.

CHEMICAL ABSTRACTS.

**Bacteriophages. II. Concentration of Lysin in its Relation to the Disappearance of the Bacteriophage Reaction.** HANS MEULI (*Z. Hyg. Infekt.-Krankh.*, 1923, **99**, 46—66; from *Chem. Zentr.*, 1923, i, 1600).—Lysin is probably not a protoplasmic poison acting in the manner of chemical disinfectants. It acts by disturbing bacterial exchanges, possibly by means of a membrane effect.  
G. W. R.

**Bacteriophages. III. Antagonistic Effect of Gelatin and Agar on the Disappearance of the Bacteriophage Reaction.** R. DOERR and W. BERGER (*Z. Hyg. Infekt.-Krankh.*, 1923, **97**, 422—432; from *Chem. Zentr.*, 1923, i, 1600).—Gelatin and other colloids such as gum and starch inhibit the bacteriophagous action of lysin. The protective action of gelatin increases with concentration, but even at the highest concentrations some effect of lysin on bacterial growth is shown.  
G. W. R.

**Utilisation of Atmospheric Nitrogen by *Saccharomyces cerevisiae*.** ELLIS I. FULMER (*Science*, 1923, **57**, 645—646).—*Saccharomyces cerevisiae*, Race F., was sub-cultured for three years at 30° in a medium containing 10 g. of sucrose, 0.188 g. of ammonium chloride, 0.1 g. of dipotassium hydrogen phosphate, and 0.1 g. of calcium chloride in 100 c.c. and then for six months in a medium containing 10 g. of sucrose, 0.188 g. of ammonium chloride, and 0.1 g. of dipotassium phosphate in 100 c.c. It was then inoculated into sterile 10% sucrose solution containing the optimal amount (0.45%) of potassium phosphate, and air free from ammonia or oxides of nitrogen was passed through the mixture. The results show that yeast will grow continuously in a medium composed of sugar and one salt, and that *S. cerevisiae* will grow in an apparently good state of nutrition, using atmospheric nitrogen as the sole source of that element. It is suggested that the beneficial effect of the aëration of yeast-cultures may be due as much to the addition of nitrogen as to that of oxygen.  
A. A. E.

**The Mechanism of Autolysis. I. The Influence of Iodine on Yeast Autolysis.** O. STEPPUN and L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1923, **140**, 17—27).—Iodine in certain concentrations accelerates the autolysis of the proteins of various yeast preparations. This action is not due to acid formation, nor is it shown by potassium iodide, and it cannot be explained on the basis of the addition of iodine to an unsaturated fatty acid with anti-proteolytic properties. Higher concentrations of iodine have an inhibiting action on the autolysis which is ascribed to the addition of iodine to the substrate.  
J. P.

**The Balance of Pyruvic Acid Fermentation.** C. NEUBERG and A. VON MAY (*Biochem. Z.*, 1923, **140**, 299—313).—The yeast fermentation of pyruvic acid, both in the presence of yeast-cells and under cell-free conditions, proceeds in accordance with the equations:  $\text{COMe}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2 + \text{CHMeO}$  and  $2\text{COMe}\cdot\text{CO}_2\text{H} \rightarrow 2\text{CO}_2 + \text{COMe}\cdot\text{CHMe}\cdot\text{OH}$ , both acetaldehyde and acetylmethylcarbinol being formed along with carbon dioxide. The acetylmethylcarbinol

was isolated as the *p*-nitrophenylosazone and the acetaldehyde as the "dimedon" compound. By quantitative measurements, the accuracy of the above formulation was confirmed. In the presence of sulphites, fermentation proceeds almost wholly as in the first equation, only traces of acetylmethylcarbinol being found. J. P.

**The Enzymatic Decarboxylation of Pyruvic Acid in a Current of Oxygen.** A. GOTTSCHALK (*Biochem. Z.*, 1923, 140, 348—352).—By the fermentation with yeast of pyruvic acid in a current of oxygen, acetaldehyde was formed in quantities as great as under anaërobic conditions. The acetaldehyde was carried over in the stream of oxygen and isolated as the bisulphite and "dimedon" compounds. J. P.

**The Fermentation of  $\alpha$ -Keto-*n*-hexoic Acid.** H. K. SEN (*Biochem. Z.*, 1923, 140, 447—452).— $\alpha$ -Keto-*n*-hexoic acid is fermented by yeast carboxylase in the presence of disodium hydrogen phosphate with the formation of carbon dioxide, *n*-valeraldehyde, and *n*-amyl alcohol. The secondary formation of amyl alcohol is inhibited by the addition of sodium hydrogen sulphite and an acetate buffer solution. J. P.

**The Destruction of Pentosans by Moulds and other Micro-organisms.** E. G. SCHMIDT, W. H. PETERSON, and E. B. FRED (*Soil Sci.*, 1923, 15, 479—488).—Studies on the destruction of pentosans in plant materials by moulds. The pentosans of wood are more rapidly destroyed in the soil than cellulose, lignin, and other cell constituents. Pentosans occur as cell constituents in fungi and may serve later as sources of carbohydrate. [See, further, *J.S.C.I.*, 1923, 1041A.] G. W. R.

**Mechanism of Oxidation in the Plant. The Oxygenase of Bach and Chodat. Function of Lecithins in Respiration.** PATRICK HUGH GALLAGHER (*Biochem. J.*, 1923, 17, 515—529).—Alcoholic extracts of plants when exposed to the air form peroxides. No evidence can be found that this formation is produced by the action of an enzyme. Minute traces of phenolic substances such as quinol or gallotannic acid usually prevent the fixation of oxygen. An autoxidisable substance of this nature isolated from fresh potato tubers was found to bear a close relation to the lipins, and it is concluded that the so-called oxygenase of the potato is an autoxidisable lecithin-like substance. Terpenes can combine with oxygen, forming a substance which can take the place of the peroxide in the peroxylase system. The blackening of aqueous extracts of the potato and of the mangold is not due to oxidation of a catechol derivative by the action of a peroxylase, but to the action of tyrosinase on tyrosine. The constituent of extract of mangold root which gives a ferric chloride coloration is a tannin. S. S. Z.

**Assimilation of Ammonia by Higher Plants.** PRIANICHNIKOV (*Compt. rend.*, 1923, 177, 603—606).—In presence of calcium carbonate, ammonium chloride is a better source of nitrogen than calcium nitrate. Of all the ammonium salts, the hydrogen carbonate is the most favourable for plant growth. E. E. T.

**The Absorption and Translocation of Lead by Plants. A Contribution to the Application of the Method of Radio-active Indicators in the Investigation of the Change of Substance in Plants.** GEORGE HEVESY (*Biochem. J.*, 1923, 17, 439—445).—The assimilation of lead by *Vicia faba* from lead nitrate solutions was estimated by a method which was based on the principle of mixing the lead solution with a radioactive isotope (thorium-B) and determining the radioactivity. The amount of lead taken up was estimated by measuring after incineration the radioactive intensity of the ash. Very small amounts of assimilated lead could be determined in this way, and it was found that whilst from 200 c.c. of a  $10^{-1}N$ -lead nitrate solution only 0.3% of the lead was taken up in the course of twenty-four hours, 60% of the lead was assimilated from a  $10^{-6}N$ -solution in the same time. The leaves were found to take up only 1% of the lead in the solution. The assimilated radioactive lead could be displaced by inactive lead when the plant was placed in a solution containing the inactive element, from which observation the author concludes that the lead is not combined with carbon in the plant, but that it exists there as a dissociable salt of low solubility. A  $10^{-1}N$ -solution of a lead salt produces a toxic effect on the plant, whilst more dilute solutions do not.

S. S. Z.

**The Effect of Different Concentrations of Manganese Sulphate on the Growth of Plants in Acid and Neutral Soils and the Necessity of Manganese as a Plant Nutrient.** J. S. MCHARGUE (*J. Agric. Res.*, 1923, 24, 781—794).—Plants grown in a carefully prepared manganese-free solution indicate the lack of manganese in the small amount of green matter produced, and in an etiolated condition of the younger leaves and buds. Seeds do not usually contain sufficient manganese to supply the needs of the plant throughout its whole growing period. Leguminous plants suffer from a deficiency of manganese more than the non-legumes. It is possible that the toxicity of acid soils may be associated in part with the presence of soluble manganese salts; but the proportion of soluble to total manganese is always small. The addition of manganese sulphate to acid soils causes a decrease in crop yields but in the presence of calcium carbonate an improved crop is obtained.

A. G. P.

**The Iron-chlorosis caused by Manganese in Green Plants.** AUGUST RIPPEL (*Biochem. Z.*, 1923, 140, 315—323).—The addition of soluble manganese salts to the cultures in which oats seedlings were growing produced a chlorosis which was remedied by the addition of iron. Since the iron content of the chlorotic and normal seedlings was the same, it is concluded that manganese does not prevent the uptake of iron by the plant, but inhibits its action after absorption.

J. P.

**The Influence of Chemical Fertilisers on the Chlorophyll Coefficient.** JEAN WLODEK (*Bull. acad. polonaise sci. let. classe sci. math. nat.*, 1920, [B], 19—52).—Determinations were made

of the chlorophyll coefficient, neochlorophyll (*A*): allochlorophyll (*B*) (Willstätter's chlorophyll *a* and *b*) by comparing the limits of the absorption bands by means of a Wagner spectrometer (*Z. Instrumentenk.*, 1913, 149). The live leaves of potato and sugar-beet were studied, grown in soils to which various fertilisers were added. It is concluded that after a certain period of development of the plants the relation of the chlorophyll pigments varies during the course of twenty-four hours; *B* increases during the day and *A* during the night. The lack of potassium results in an absolute and relative diminution of *B* and an increase in *A*, as well as a reduction of the daily variation of the two components. Lack of phosphorus also reduces the daily variation of the chlorophyll components and narrows the absorption bands; nitrogen tends to reduce *A* and augment *B*. The action of calcium and magnesium is not definitely established.

CHEMICAL ABSTRACTS.

**The Influence of Light and of Chemical Fertilisers on the Chlorophyll Coefficient.** JEAN WLODEK (*Bull. acad. polonaise sci. let. classe sci. math. nat.*, 1921, [B], 143—90; cf. preceding abstract).—The variations of the chlorophyll coefficient in *Iris germanica* under the influence of light with attached and excised leaves were studied. During illumination, the absorption bands shift toward the more refrangible portion of the spectrum and in the opposite direction in the dark. In illuminated leaves the absorption band of allochlorophyll becomes wider, that of neochlorophyll narrower, whilst the reverse happens in the dark. This change requires three-quarters of an hour to two hours. The shifting of the absorption band is noticeable after fifteen minutes. Leaves which have died through wilting show an increased chlorophyll coefficient and a shifting of the absorption band towards the violet. Ether diminishes the variations in the chlorophyll coefficient. With a lack of potassium the coefficient diminishes at a certain phase of development of oats, barley, and beans. This is due to an increase of the absorption band of neochlorophyll and a decrease in that of allochlorophyll, as compared with plants grown under normal conditions. A lack of nitrogen in the soil increases the chlorophyll coefficient. A relation seems to exist between the width of the first absorption band and the nitrogen content in fresh bean leaves, in the straw and harvest of oats and barley. The nitrogen content increases with the width of the band. With a lack of potassium, the chlorophyll coefficient does not change under the influence of light and dark. In leaves which show an abnormal chlorophyll coefficient the production of vegetative material is less.

CHEMICAL ABSTRACTS.

**The Physiological Significance of Titanium in the Plant Organism.** ANTONÍN NĚMEC and VÁCLAV KÁŠ (*Biochem. Z.*, 1923, 140, 583—590).—By the addition of sodium titanate or sodium titanocitrate ( $\text{Na}_2\text{TiO}_3 \cdot \text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) to the earth in which mustard, pea, and lucerne plants were grown, a 30—40% increase in growth over controls was obtained. The magnitude of the increase ran

parallel to the amount of titanium absorbed. The iron content of the plants diminished with increasing uptake of titanium, and the other mineral constituents showed variations more or less marked.  
J. P.

**Pectin and its Hypothetical Precursor "Protopectin."**  
FRANK TUTIN (*Biochem. J.*, 1923, 17, 510—514).—Unripe apple tissue was repeatedly disintegrated and extracted with alcohol and with water in order to remove the pectin. On heating the residual marc in an autoclave at 110° with  $N/20$ -hydrochloric acid, only an insignificant quantity of pectin was obtained. The author concludes that "protopectin" does not exist, and that all the pectin present in the apple occurs in ordinary soluble form. The persistent retention of pectin in an insoluble form by the tissue of unripe fruit is due partly to the presence in it of a substance insoluble in water but soluble in alcohol and partly to the difficulty of the disintegration by mechanical means of the unripe tissue. Hence "protopectin" is not the cause of the hardness of the tissue of unripe fruit.  
S. S. Z.

**Presence of Maltase in Germinated and Ungerminated Barley.** ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*Biochem. J.*, 1923, 17, 593—596).—Malts, whether green or kilned, obtained by germinating barley hydrolyse maltose (cf. Daish, A., 1916, i, 535). The intensity of the action of the enzyme depends on the temperature and on the way in which the malt has been heated. Ungerminated barley also contains an enzyme capable of producing dextrose from maltose. This reaction can only be obtained by employing ground barley, as the enzyme cannot be extracted with water. This enzyme is also destroyed by alcohol, and therefore diastase preparations obtained by cold water extraction of malt and precipitation of the aqueous extract with alcohol do not hydrolyse maltose.  
S. S. Z.

**The Hydrogen-ion Concentration of the Soil in Relation to the Flower Colour of *Hydrangea hortensis*, W., and the Availability of Iron.** W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1923, 17, 201—210).—The flowers of *Hydrangea hortensis* are blue when the plant is grown in acid soil,  $p_H$  5.7 to 6.0 or slightly above, pink with  $p_H$  7.5 or above, whilst if the  $p_H$  value of the soil lies between these values, blue and pink flowers may be present on the same plant. The flower pigment is not here acting as an indicator, for the  $p_H$  of both kinds of flower is about 4.2. There is strong evidence that blue flowers only occur when ferrous iron is available. Ferrous salts remain in solution after ferric salts are completely precipitated. Precipitation of ferrous hydroxide starts at about  $p_H$  5.1, and is not complete at 7.1. The blue flowers are found to contain considerably more iron than the pink flowers, the proportions being 140 and 60 parts per million of dried flower, respectively. Treatment of soils with alum or aluminium sulphate solution causes the formation of blue hydrangeas. These solutions

have  $p_H$  3.6 to 4.0, and may well increase the availability of iron. It may be, however, that aluminium as well as iron may form a blue complex with the pink anthocyanin. The occurrence of chlorosis in plants grown on alkaline soil may be due to the non-availability of iron.

E. H. R.

**Presence of Maltose in *Mercurialis perennis*.** P. GILLOT (*J. Pharm. Chim.*, 1923, [vii], 28, 148—154; cf. A., 1922, i, 1101).—The dextrorotatory sugar present, together with sucrose, in the rhizomes of *Mercurialis perennis* is maltose. The amount increases during the summer months to a maximum of about 2% in September and then decreases, the minimum of 0.25% being reached in April.

W. P. S.

**Formation of Maltose in Sweet Potatoes on Cooking.** H. C. GORE (*Ind. Eng. Chem.*, 1923, 15, 938—940).—The presence of maltose in cooked sweet potatoes is shown by the agreement of the quantity of sugars as determined by copper reduction with the quantities measured by polarisation and by its isolation in crystalline form. Sugar is not formed at the boiling point, but is produced very rapidly, although not instantaneously, by diastatic action during the initial stages of the digestion. The increase in sugar calculated as maltose caused by cooking in steam, baking, or boiling varied from 11.5% to 17%.

H. C. R.

**Odorous and Bitter Constituents of Neem Oil.** EDWIN ROY WATSON, NITYA GOPAL CHATTERJEE, and KSHITISH CHANDRA MIKBERJEE (*J. Soc. Chem. Ind.*, 1923, 42, 387—389t).—By saponification of neem oil (from *Melia azadirachta*) and repeated salting out of the resulting soaps, the bitter constituents are obtained in the lys, from which they are precipitated as a resin by acidifying. From this resin, after extraction of some free sulphur with benzene, an amorphous bitter substance,  $C_{15}H_{20}O_5$ , and a crystalline bitter substance, *margosopicrin*,  $C_{24}H_{32}O_8$ , were obtained. The latter forms rhombic prisms, m. p. 221—222° after swelling at 128°. It has  $[\alpha]_D^{20} +163.8^\circ$ , and from the properties of its acetyl derivative would appear to be  $OH \cdot C_{23}H_{24} \cdot CO_2H \cdot 3H_2O$ . *Acetylmargosopicrin*,  $Ac \cdot C_{23}H_{24}O_2 \cdot CO_2H$ , forms colourless needles, m. p. above 280°; it is devoid of bitterness, which, however, can be regenerated by hydrolysis. The odorous constituent, obtained by steam distillation if the oil (?  $C_{21}H_{44}S$ ), was not obtained in a pure state; it is not a mercaptan. On boiling neem seeds with water, precipitating the extract with basic lead acetate, and concentrating the filtrate, an odorous substance of composition  $C_{13}H_{24}O_4S_2$  is obtained; it forms rectangular prisms, m. p. above 230°, and has  $[\alpha]_D^{20} -325^\circ$ . On prolonged boiling with dilute hydrochloric acid, hydrogen sulphide is evolved and the solution becomes reducing to Fehling's solution.

G. W. R.

**Cultural Experiments in France—Peppermint and Lavender.** ERNEST AUTRAN and LOUIS FONDAND (*Perf. Essent. Oil. tec.*, 1923, 14, 334—335).—Red peppermint oil was obtained

containing 7.07% menthyl acetate and 83.2% menthol. The figures for white peppermint oil were 12.37% and 60.6% respectively. Of the lavender oils, the "blue" showed  $\alpha - 10^\circ 12'$  with 44.4% esters, and the "white"  $\alpha - 9^\circ 5'$  with 58.6% esters. A. G. P.

**The Effect of Respiration on the Protein Percentage of Wheat, Oats, and Barley.** F. W. MCGINNIS and G. S. TAYLOR (*J. Agric. Res.*, 1923, 24, 1041—1048).—The loss of carbohydrate material of grain during the ripening stage was measured by the amount of carbon dioxide evolved during respiration. This loss was found to be considerable, the maxima occurring just before the drying off of the grain, i.e., when the moisture content is of the order of 40%. The loss of carbohydrate would appear markedly to influence the protein content of the grain, although other factors were doubtless concerned. Variations in protein were greatest in wheat, followed, in order, by barley and oats. A. G. P.

**Factors Affecting the Nitrogen Content of Wheat and the Changes that occur during the Development of Wheat.** GEORGE A. OLSON (*J. Agric. Res.*, 1923, 24, 939—953).—The nitrogen content of wheat was determined during growth under varying conditions. By increasing the width apart of the rows, higher nitrogen contents of wheat were obtained in non-irrigated land. On irrigated land, however, no differences were observed. During the formation and early maturing stages of the grain, the nitrogen of the plant moved upwards. As the grain matured, its nitrogen content decreased. The nitrogen content of wheat was not affected by irrigation, but the placing of the plant in water caused a movement of nitrogen into the grain. The actual grain ceased to increase in weight when the soil moisture content fell below 40%. After the initial stages of growth, the intake curves for nitrogen and phosphorus were almost identical in character. A. G. P.

**The Occurrence of Polypeptides and Free Amino-acids in the Ungerminated Wheat Kernel.** S. L. JODIDI and K. S. MARKLEY (*J. Amer. Chem. Soc.*, 1923, 45, 2137—2144).—It is shown that the following varieties of ungerminated wheat kernel, Kanred, Fultz, Marquis, and Kubanka, contain nitrogen as amides, free amino-acids, and polypeptides.

The presence of amino-acids is demonstrated by the following procedure. The clear, filtered extract, obtained by digesting the "whole wheat" flour, ground to pass a 40-mesh sieve, with cold water for two hours, is concentrated on the water-bath. During this process a precipitate, apparently proteins, is formed, and is removed by centrifuging. The liquid is taken to dryness, and the non-protein matter extracted from the residue by means of 70% alcohol, the latter being then removed from the filtered extract. The residue, a yellow syrup, is dissolved in hot water; the total nitrogen is estimated in part of the solution, by Kjeldahl's method, whilst another part of the solution is freed from carbon dioxide, phosphorus

acid, and colouring matter, and titrated with formol (cf. Jodidi, A., 1911, ii, 820; 1912, ii, 292; 1918, ii, 379). Since proteins may not be completely removed by this method, it is modified as follows. The boiling, aqueous solution of the dried alcoholic extract is treated successively with acetic acid, and with freshly prepared lead hydroxide and lead acetate; the liquid is boiled and filtered after each treatment. The clear solution is concentrated, and treated as before. Both these methods are further modified by conducting the evaporations under reduced pressure.

Amides, and other substances containing ammoniacal nitrogen, are estimated by estimating the total nitrogen, by Kjeldahl's method, in the aqueous solution of the dried alcoholic extract, and then estimating the nitrogen evolved as ammonia, when the solution is treated with hydrochloric acid to a final concentration of 20% and boiled for thirty minutes. This corresponds with the amides; the further quantity of ammonia eliminated when the hydrolysis is continued for twelve hours corresponds with the other ammoniacal substances.

Polypeptides present in the wheat kernel must, when hydrolysed long enough, yield free amino-acids. Hence they may be estimated by determining the increase in amino-acid content after hydrolysis. The boiling aqueous solution of the dried alcoholic extract is treated successively, as above, with acetic acid, lead hydroxide, and lead acetate. The nitrogen in the final, clear solution is estimated by Kjeldahl's method. A portion of the solution is then treated with hydrochloric acid, to give a final concentration of 20%, boiled for twelve hours, and taken to dryness. The residue is distilled with a cream made by grinding magnesium oxide with water (Jodidi and Moulton, A., 1919, i, 603). The aqueous extract of the magnesium oxide residue is then analysed by Kjeldahl's method, and by formol titration.

The following method is devised to remove proteoses and peptones, if present. The aqueous solution of the dried alcoholic extract is treated with sulphuric acid and phosphotungstic acid. After keeping for twenty-four hours, the precipitate is removed and washed with a solution of the same reagents. The filtrate is freed from sulphuric and phosphotungstic acids by treatment with barium hydroxide, the excess of which is removed by means of carbon dioxide. The filtered liquid is concentrated, and the peptide nitrogen estimated after hydrolysing with hydrochloric acid.

Kanred, Fultz, Marquis, and Kubanka ungerminated wheat kernels contain peptide nitrogen in the following percentages, respectively: 26.86, 28.09, 32.20, and 37.76%, on the basis of water-soluble nitrogen, or 3.89, 4.67, 4.98, and 5.13%, calculated to the total nitrogen. The figures for amino-acid nitrogen are, approximately, 16, 11, 11, and 10%, calculated to the water-soluble nitrogen, and 2.3, 1.8, 1.8, and 1.4%, calculated to the total nitrogen. Amide nitrogen is present to the following extent: 12.99, 8.76, 12.33, and 12.61%, on the basis of water-soluble nitrogen, or 1.88, 1.46, 1.91, and 1.72%, calculated to the total nitrogen. W. S. N.

**The Litmus Paper Method for Detecting the Soil Reaction.** EVERETT A. CARLETON (*Soil Sci.*, 1923, 16, 91—94).—The results of the litmus paper test with soils depend on their hydrogen-ion concentration. The arrangement of a series of soils in order of increasing acidity, using the litmus paper test by two observers, showed a fair agreement with  $p_H$  figures, obtained electrometrically. A soil cannot be assumed to be basic if it does not impart the full blue colour to litmus paper. Soils which do not show acidity by the litmus paper test may yet show a lime requirement by the calcium acetate method. G. W. R.

**Influence of the Absolute Reaction of a Soil on its Azotobacter Flora and Nitrogen-fixing Ability.** P. I. GAINNEY (*J. Agric. Res.*, 1923, 24, 907—938).—The examination is recorded of a large number of soils, for the presence and activity of nitrogen-fixing organisms. The results of previous laboratory researches were confirmed; few soils with  $p_H$  lower than 6.0 contained *Azotobacter*, whilst in nearly all soils having  $p_H$  greater than 6.0 *Azotobacter* were observed. The possibility is noted that the reaction of the soil may well be the limiting factor governing the growth of *Azotobacter*. Soil reactions determined electrically agreed well with those found by Gillespie's modification of the indicator method. In general, the electrometric method indicated slightly higher hydrogen-ion concentrations on the acid side, and lower on the alkaline side, as the actual values diverged from the neutral point. A. G. P.

**Soil Reaction.** P. E. KARRAKER (*Soil Sci.*, 1923, 15, 473—478).—Data are given for soil reaction, determined by the electrometric method, lime requirement by Veitch and Hopkins's methods, and yields of clover hay, for a number of plots with different manurial treatments. The correlations observed are in general agreement with current hypotheses. Similar results were obtained in a series of experiments with sweet clover. G. W. R.

**A Modification of the Truog Soil Acidity Test.** F. W. PARKER and J. W. TYDMORE (*Soil Sci.*, 1923, 16, 75—78).—The Truog soil acidity test is modified so that the hydrogen sulphide evolved is collected and estimated volumetrically. [See, further, *J.S.C.I.*, 1923, 1035A.] G. W. R.

**Oxygen-supplying Power of the Soil as Indicated by Colour Changes in Alkaline Pyrogallol Solution.** LEE M. HUTCHINS and BURTON E. LIVINGSTONE (*J. Agric. Res.*, 1923, 25, 133—140).—The apparatus consisted of a porous porcelain cylinder soaked in paraffin oil and having a pair of leading-in tubes sealed passing in through a stopper closing the open end of the cylinder. Oxygen from the soil in which the cylinder was buried diffused into the cylinder and was swept out into wash-bottles containing alkaline pyrogallol by a continuous current of inert oxygen-free gas, e.g., coal gas. Experiments with this apparatus indicated that the

oxygen-supplying power of a soil is greater nearer the surface, and is decreased by excessive moisture and close packing. [Cf. *J.S.C.I.*, 1923, Nov.]  
A. G. P.

**Effect of Season on Nitrification (in Soils).** BRUNO SCHÖNBRUNN (*Zentr. Bakt. Par.*, 1922, 56, ii, 545—565, from *Chem. Zentr.*, 1923, i, 1606).—From ammonification and nitrification experiments on soils with temperature control, it is concluded that there is no inherent periodicity in these processes in the soil apart from that due to changes in temperature and other factors.

G. W. R.

**Effect of Season on Nitrification in Soils.** F. LÖHNIS (*Zentr. Bakt. Par.*, 1923, 58, ii, 207—211; from *Chem. Zentr.*, 1923, i, 1606—1607).—Criticism of Schönbrunn's conclusions (see preceding abstract). The author contends that there is a seasonal effect in nitrification.

G. W. R.

**The Occurrence and Action of Fungi in Soils.** ERNEST V. ABBOTT (*Soil Sci.*, 1923, 16, 207—216).—Twenty-eight species of fungi representing twelve genera were isolated from five Iowa soils of varying lime requirement. With two exceptions all the species showed vigorous ammonifying power.

G. W. R.

**Partial Sterilisation of Soil. Microbiological Activities and Soil Fertility.** SELMAN A. WAKSMAN and ROBERT L. STARKY (*Soil Sci.*, 1923, 16, 137—158).—Experiments on the effect of treatment with toluene, and of heat on soils are described. Partial sterilisation affects not only bacteria and protozoa but also fungi and actinomycetes. Whilst protozoa may limit bacterial development in abnormal soils such as greenhouse soils, such an inhibition is held to be improbable in ordinary soils. [See, further, *J.S.C.I.*, 1923, Nov.]

G. W. R.

**Distribution of the Phosphorus-ion in the Upper Layers of the Soil in Relation to Vegetation and the Addition of Various Salts.** G. LEONCINI and F. A. ROGAI (*Agr. Italiana*, 1922, 45, Nos. 4—6, 109—124).—The effect exerted by vegetation or soluble salts on the known adsorption of added phosphate in the surface layers of irrigated soils is, in general, to render the distribution of the phosphorus-ion more uniform, hence causing deeper penetration, and to increase the soluble phosphate-fixing power of the soil. An attempt to determine the specific effects of anions and kations was unsuccessful.

CHEMICAL ABSTRACTS.

**The Fixation of Phosphoric Acid by the Soil.** G. S. FRAPS (*Texas Agr. Expt. Sta. Bull.*, 1922, No. 304).—The fixation of phosphoric acid from dilute solutions of dipotassium hydrogen phosphate was usually increased with time of contact, and in some cases by increase of temperature, whereas treatment with acid often caused a decrease. Ignition increased the fixing power. Percolation experiments indicated that, under natural conditions,

heavy rains would be required to cause any loss of phosphoric acid even from soils of low fixing power. The active phosphoric acid was found to increase with the absorbing power until the latter reached 40–60%, and then to decrease. The acid consumed and the calcium oxide increased until the absorption was 60–80% and then decreased. The iron and aluminium oxides, however, increasing with the phosphoric acid fixed, were found to have a much greater influence on the fixation.

CHEMICAL ABSTRACTS.

**Comparison of the Jones Calcium Acetate Method for Lime Requirement with the Hydrogen-ion Concentration of some Quebec Soils.** EVERETT A. CARLETON (*Soil Sci.*, 1923, 16, 79–90).—A general correlation was observed between soil reaction, determined electrometrically and colorimetrically, and lime requirement by the Jones calcium acetate method. [See, further, *J.S.C.I.*, 1923, Nov.]

G. W. R.

**Effect of Addition of Calcium and Magnesium on the Outgo of Sulphates in Leachings from a Loam Soil.** W. H. MACINTYRE, W. M. SHAW, and J. B. YOUNG (*Soil Sci.*, 1923, 16, 1–40).—Applications of the oxides and carbonates of calcium and magnesium, ground limestone, dolomite, and magnesite, all cause an increase in the loss of sulphates by leaching from surface soil. The rate of loss diminishes after the first year. Excessive applications of calcium oxide depress the losses of calcium sulphate. [See, further, *J.S.C.I.*, 1923, 1036A.]

G. W. R.

**The Transient Nature of Toxicity induced by Magnesium and its Bearing upon Lime-Magnesia Ratio Studies.** W. H. MACINTYRE and J. B. YOUNG (*Soil Sci.*, 1923, 15, 427–461).—Lysimetric studies over a period of years with tall oat grass and cowpeas grown in cylinders of soil with different dressings of calcium and magnesium compounds are reported. An initial toxic effect which subsequently disappeared was observed where precipitated magnesium carbonate was used. Dolomite showed no toxic effect and was as beneficial as limestone. The initial toxicity due to magnesium compounds and its subsequent disappearance are discussed. The authors suggest that the initial reaction whereby magnesium carbonate is rapidly converted into relatively soluble silicate combinations is succeeded by a slow change into more complex and less soluble combinations. Attention is directed to the necessity for using cultures in soil extending over several seasons when studying the effect of magnesium carbonates on plant growth.

G. W. R.

## Organic Chemistry.

**The Extraction of Mineral Oils with Methyl Alcohol.** HANS STÄGER (*Helv. Chim. Acta*, 1923, 6, 893—900).—To investigate the cause of sludge formation in transformer oils (cf. this vol., i, 649), the author extracted a number of such oils with methyl alcohol and submitted the extracts and the extracted oil to the usual tests for such oils. The alcohol extracted from the oil the unsaturated cyclic compounds, and the extracts when oxidised with sodium peroxide showed high acidity. The extracted oils, however, still showed considerable sludge formation when heated for a long period at 112° in presence of copper. [Cf. *J.S.C.I.*, 1923, 1117A.]

E. H. R.

**Density of Acetylene.** JITSUSABURO SAMESHIMA and KOICHI FUKAYA (*J. Chem. Soc. Japan*, 1923, 44, 690—708).—It has been found that acetylene behaved differently from other gases when the velocity of diffusion of methane, ammonia, acetylene, nitrogen, carbon monoxide, air, oxygen, and carbon dioxide through an unglazed porcelain plate, and through a perforated platinum plate, was measured at various pressures. The behaviour of acetylene may be explained by assuming that it undergoes molecular association at high pressure. The density of acetylene was therefore measured at 0° and 25° under pressures from 0.3858 to 2.3764 atmosphere by Dumas' method, and an equilibrium,  $(C_2H_2)_2 \rightleftharpoons 3C_2H_2$ , was established. The equilibrium constant at 0° is 319.1 and that at 25° 509.7, so the heat of dissociation  $(C_2H_2)_2 \rightleftharpoons 3C_2H_2$ —3027 cal.

K. K.

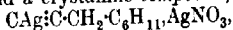
**Contact Polymerisation of Acetylene.** N. D. ZELINSKI (*Compt. rend.*, 1923, 177, 882—885).—The well-known conversion of acetylene into benzene has hitherto only been effected with very small quantities of material. If, however, acetylene is passed through a tube filled with activated wood-charcoal, and heated at 640—650°, 70—80% of the gas is converted into a tar, of which, by weight, 45% boils at 20—150°, 13.9% at 150—250°, 29% at 104—300°/13 mm., 12% remaining as a residue. Of the lowest fraction, 40% boils at 79—115°, and is mainly benzene, containing toluene and xylene. The fraction boiling at 79—80°/738 mm. has  $d_4^{20}$  0.8857,  $n_D^{20}$  1.504, and after purification with concentrated sulphuric acid gives pure benzene (about 35% of total tar), b. p. 79.6°/747.5,  $d_4^{20}$  0.8790,  $n_D^{20}$  1.49678,  $n_D^{25}$  1.50148,  $n_F^{20}$  1.51350,  $n_D^{20}$  1.52375. Toluene (4%), *p*-xylene (0.4%), styrene, and indene may be isolated in the pure state, whilst naphthalene (6.7%), fluorene (1%), and much anthracene are isolable after repeated recrystallisation.

E. E. T.

**Double Decompositions, in Aqueous Media, between Metallic Acetylides and Salts.** J. F. DURAND (*Compt. rend.*, 1923, 177, 693—695).—When calcium carbide is added to an aqueous solution of cupric or mercuric chloride, the corresponding acetylide,  $\text{CuC}_2$  or  $\text{HgC}_2$ , is precipitated, together with the hydroxide, etc. With silver nitrate, calcium carbide gives an explosive precipitate, presumably of the compound  $\text{Ag}_2\text{C}_2\cdot\text{AgNO}_3$ , whilst with normal lead acetate it gives a precipitate containing *plumbous acetylide*,  $\text{PbC}_2$ , as a grey powder stable to air and water, and giving acetylene when treated with hydrochloric acid. From ferrous, nickelous, cobaltous, and manganous chloride solutions, calcium carbide precipitates the impure *acetylides*,  $\text{FeC}_2$ ,  $\text{NiC}_2$ ,  $\text{CoC}_2$ , and  $\text{MnC}_2$ , respectively. Mercuric acetylide with aqueous silver nitrate gives silver acetylide, but with cupric chloride or nitrate it gives no precipitate. With mercurous nitrate solution, mercurous acetylide is formed. Cuprous acetylide affords an explosive mixture of silver and silver acetylide with aqueous silver nitrate, and a mixture of mercury and mercurous acetylide with aqueous mercurous nitrate. Cupric acetylide with silver nitrate gives silver acetylide, and with mercurous nitrate, mercurous acetylide. Silver acetylide has no action on aqueous solutions of cupric, mercurous, or mercuric nitrates.

E. E. T.

**Preparation of True Acetylene Hydrocarbons from  $\beta$ -Dibromopropylene, using Sodamide: True Hexinene and cyclohexylpropinene.** BOURGUEL (*Compt. rend.*, 1923, 177, 688—690; cf. this vol., i, 429, and Lespieau, A., 1921, i, 656, etc.).—The interaction of Grignard reagents and  $\beta$ -dibromopropylene gives better yields of  $\beta$ -bromo- $\Delta^a$ -alkylenes if the magnesium derivative is added to excess of the dibromo-compound. Magnesium ethyl and *n*-propyl bromides, respectively, gave  $\beta$ -bromo- $\Delta^a$ -pentene and  $\beta$ -bromo- $\Delta^a$ -hexene (b. p.  $134^\circ/760$  mm.,  $d^{20}_4$  1.203,  $n^{20}_D$  1.455), the latter, with sodamide, affording *n*- $\Delta^a$ -hexinene, b. p.  $70$ — $71^\circ$ . Magnesium phenyl and magnesium cyclohexyl bromides similarly led to the preparation of  $\beta$ -bromo- $\gamma$ -phenyl- $\Delta^a$ -propene and  $\beta$ -bromo- $\gamma$ -cyclohexyl- $\Delta^a$ -propene, the properties of the latter now being determined accurately (b. p.  $84$ — $85^\circ/10$ — $11$  mm.,  $d^{20}_4$  1.125,  $n^{20}_D$  1.495), and its conversion into  $\gamma$ -cyclohexyl- $\Delta^a$ -propinene (b. p.  $48^\circ/12$  mm. or  $157^\circ$  [corr.]/ $760$  mm.,  $d^{20}_4$  0.836,  $n^{20}_D$  1.459) repeated. This hydrocarbon gives a yellow precipitate with ammoniacal cuprous chloride, and a crystalline compound,



with silver nitrate.

E. E. T.

**The Action of Aluminium Chloride on Trichloroethylene.** FELIX KAUFLEDER (*Annalen*, 1923, 433, 48—51).—The action of aluminium chloride on boiling trichloroethylene causes condensation, with elimination of hydrogen chloride and the formation of two isomeric *tetrachlorobutadienes*. The first has b. p.  $193$ — $198^\circ/720$  mm.,  $d^{20}_4$  1.622, and the second b. p.  $198$ — $200^\circ/720$  mm.,  $d^{20}_4$  1.634. Their chemical properties are similar. Oxygen at temperatures up to  $100^\circ$  has no action; zinc has no action. Chlorine

is not perceptibly taken up at 60° in the presence of sulphur or iodine, but at 110° in the presence of ferric chloride (10%) an increase in weight of 44% is observed after ten hours. The product is almost entirely hexachloroethane.

W. S. N.

**The Alkylglycerols.** R. DELABY (*Ann. Chim.*, 1923, [ix], 20, 196—232; cf. this vol., i, 993).—The action of industrial (88%) formic acid on ethylglycerol results in the formation of a mixture of mono-, di-, and tri-formins together with unchanged alcohol. If, however, 96% acid is employed, the reaction-mixture yields *ethylglycerol triformin*, needles, m. p. 55—56°, on distillation at 155—158°/20 mm. Addition of a crystal to the mixture of formins causes crystallisation of this substance to take place; further, on heating the mixture at a temperature gradually increasing to 270° and distilling the residue at 136—140°/12 mm., the same substance is obtained. The distillate resulting from the decomposition of the mono- and di-formins contains a mixture of water,  $\beta$ -ethylallyl formate, and the formin of vinyl ethylcarbinol from which the alcohols may be obtained by saponification followed by careful fractionation. A suggestion as to the mechanism of formation of these alcohols and their formins by loss of water and of carbon dioxide from the three isomeric monoformins and the three possible isomeric diformins is made.

Catalytic dehydration of ethylglycerol over anhydrous magnesium sulphate leads to the formation of a complex mixture of substances, among which acetaldehyde, ethyl vinyl ketone, and a furan derivative of unknown constitution were identified (cf. following abstract). The following are described:  $\Delta^2$ -pentene- $\alpha$ -ol, ( $\beta$ -ethylallyl alcohol), b. p. 141—142° (corr.),  $d_4^{20}$  0.8645,  $d_4^{25}$  0.8554,  $n_D^{20}$  1.43787; *allophanate*, crystalline powder, m. p. 157—157.5°.  $\Delta^2$ -Penten- $\alpha$ -aldehyde ( $\beta$ -ethylacetaldehyde),  $\text{CH}_2\text{Et}\cdot\text{CH}\cdot\text{CHO}$ , a mobile lachrymatory liquid, b. p. 139°,  $d_4^{20}$  0.867,  $d_4^{25}$  0.854,  $n_D^{20}$  1.4387; *semicarbazone*, needles, m. p. 177—178°.

H. J. E.

**Catalytic Dehydration of Ethylglycerol.** RAYMOND DELABY (*Compt. rend.*, 1923, 177, 690—693; cf. this vol., i, 753).—The catalytic dehydration of ethylglycerol (using anhydrous magnesium sulphate at 340—360°), which could theoretically give rise to  $\Delta^2$ - and  $\Delta^3$ -pentaldehydes,  $\Delta^2$ -penten- $\beta$ -one,  $\Delta^2$ -penten- $\gamma$ -one (ethyl vinyl ketone),  $\Delta^2$ -pentadiene- $\alpha$ -ol, and various compounds of lower carbon-content: actually affords a mixture of acetaldehyde, furan derivatives, and ethyl vinyl ketone, the latter being detected by its behaviour towards semicarbazide (cf. Maire, A., 1908, i, 290). Thus, whilst the above pentaldehydes and  $\Delta^2$ -penten- $\beta$ -one give crystalline derivatives when treated with semicarbazide, the product of the above dehydration gives sparingly soluble, amorphous derivatives, characteristic of vinyl ketones. The same product, with hydrazine hydrate, gives *dihydrazinoethylvinylketazine*,



volatile, scaly crystals, m. p. 80—81°.

It is thus probable that the homologues of acetaldehyde cannot

be prepared by the catalytic dehydration of the homologues of glycerol. E. E. T.

**Alkyl Hypochlorites.** FREDERICK DANIEL CHATTAWAY and OTTO GUIDO BACKEBERG (T., 1923, 123, 2999—3003).

**Molecular Compounds of Orthophosphoric Acid and Ethyl Ether.** MARK RABINOWITSCH and SOPHIE JAKUBSOHN (Z. anorg. Chem., 1923, 129, 55—59).—The system ortho-phosphoric acid-ethyl ether was investigated between 0.0 and 17.50% ether by the method of thermal analysis. The existence of the following two compounds was indicated:  $6\text{H}_3\text{PO}_4 \cdot \text{OEt}_2$ , m. p.  $28.2^\circ$ , and  $4\text{H}_3\text{PO}_4 \cdot \text{OEt}_2$ , m. p.  $30.0^\circ$ . W. T.

**Process for Producing Formic Acid Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (Brit. Pat. 203812).—Formamide is obtained by the interaction of carbon monoxide and ammonia at high pressures and temperatures exceeding  $100^\circ$ . In the presence of water, formamide and ammonium formate, or the latter alone, are produced. Catalysts may be employed to accelerate the reaction. [Cf. J.S.C.I., 1923, Dec.] W. T. K. B.

**Separation of Octoic and Decoic Acids from Coconut Oil.** ERIC EVERARD WALKER (T., 1923, 123, 2837—2839).

**New Method for the Reduction of Esters.** H. J. PRINS (Rec. trav. chim., 1923, 42, 1050—1052).—The ester is dissolved in ether, and saturated sodium acetate is added to form a bottom layer. The temperature is kept at about  $-5^\circ$  and sodium and 80% acetic acid are added in sufficient quantity to keep the ether slightly acid. If allowed to become alkaline, the ester is hydrolysed, whilst an acid solution increases the evolution of gaseous hydrogen at the expense of reducing hydrogen. The reaction for 0.5 kg. lots takes from three to five days, and about 30% excess of sodium is required. It is supposed that aldehyde is first formed and then is reduced to alcohol on the surface of the metal. The yield is about 90% with aliphatic acids, but only about 50% with phenyl acetic acid. H. H.

**The Conversion of Paraformaldehyde into Glycollic Acid.** DALZIEL LLEWELLYN HAMMICK and ALFRED REGINALD BOEREE (T., 1923, 123, 2881—2882).

**Acetone Compounds of  $\alpha$ -Hydroxy-acids.** RICHARD WILLSTÄTTER and FRANZ KÖNIGSBERGER (Ber., 1923, 56, [B], 2107—2109).—The ketonic compounds of  $\alpha$ -hydroxy-acids can be obtained directly from their components under the influence of hydrogen chloride, sulphuric acid, or copper sulphate. In the series glycollic, mandelic, benzoic acids, the reactivity towards acetone and the stability of the acetone compounds increases with increasing substitution of the carbinol group.

Acetone-glycollic acid,  $\begin{array}{c} \text{CH}_2\text{CO} \\ | \\ \text{O}-\text{CMe}_2 \end{array} > \text{O}$ , is obtained under definite conditions by the addition of concentrated sulphuric acid to a

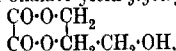
solution of glycollic acid in acetone at  $-5^{\circ}$ ; it is a colourless liquid, b. p.  $41^{\circ}$ /about 11 mm.,  $d_4^{20}$  1.0857, which is extremely readily hydrolysed by water. *Acetone-r-mandelic acid* form colourless crystals, m. p.  $47.5-48^{\circ}$ , b. p.  $135^{\circ}$ /about 11 mm.; it is decomposed into mandelic acid slowly when preserved in a closed vessel, and moderately rapidly when exposed to the air of the laboratory. *Acetone-d-mandelic acid* has m. p.  $73.5^{\circ}$ ,  $[\alpha]_D^{20} +94.41^{\circ}$ , when dissolved in ethyl acetate, whereas the *l-isomeride* has m. p.  $73.5^{\circ}$ ,  $[\alpha]_D^{20} -94.78^{\circ}$  in ethyl acetate solution. *Acetone-benzilic acid*,  $C_{15}H_{16}O_3$ , forms cubic crystals, m. p.  $48^{\circ}$ .  
H. W.

**Inorganic Complex Salts. III. Racemisation and the Stability of Complex Ions.** WILLIAM THOMAS and RONALD FRASER (T., 1923, 123, 2973-2976).

**The Dissociation of Certain Oxalato-salts.** GEORGE JOSEPH BURROWS and GEORGE WALKER (T., 1923, 123, 2738-2742).

**Thermal Decomposition of Ethylene Oxalate.** M. TILITSCHEV (Ber., 1923, 56, [B], 2218-2222).—Ethylene oxalate,  $CO \cdot O \cdot CH_2$ , m. p.  $160-162^{\circ}$ , b. p. about  $175^{\circ}/5$  mm., is prepared from ethylene glycol and methyl oxalate. It decomposes at  $241^{\circ}$  to the extent of about 40% into ethylene and carbon dioxide, and to about 28% into ethylene carbonate and carbon monoxide. The remainder (about 24%) yields products which are very difficult to identify; it probably contains acetaldehyde in a combined form.

Glycerol and methyl oxalate yield *glyceryl oxalate*,



a hard, glassy substance, m. p.  $220-225^{\circ}$  (decomp.). Allyl alcohol, carbon monoxide, and carbon dioxide are found among the products of its decomposition by heat.  
H. W.

**Ring-chain Tautomerism. VII. The  $\alpha\beta$ -Trisubstituted Glutaric Acid Type.** KANTILAL CHHAGANIL PANDYA and JOCELYN FIELD THORPE (T., 1923, 123, 2852-2865).

**The Formation of Stable  $\beta$ -Lactones.** LESLIE BAINS and JOCELYN FIELD THORPE (T., 1923, 123, 2742-2745).

**Optical Activation of Racemic Acid by *d*-Malic Acid.** ALEX. MCKENZIE, HAROLD JAMES PLENDERLEITH, and NELLIE WALKER (T., 1923, 123, 2875-2880).

**A Condensation Product from Four Acetoacetic Ester Molecules,  $\alpha$ -(4-Carboxy-3:5-dimethylphenyl)- $\beta$ -methylglutaconic Acid.** FRANZ FEIST [with ERICH EGGERT] (*Annalen*, 1923, 433, 51-64).—By the action of concentrated alkali on ethyl isodehydracetate, Anschütz, Bendix, and Kerp (A., 1891, 172) obtained two acids, having m. p., respectively,  $149^{\circ}$  and  $234^{\circ}$ . The latter has already been shown to be tribasic, and to have the formula  $C_{15}H_{16}O_8$  (Feist and Beyer, A., 1906, i, 334). It is now shown to be  $\alpha$ -(4-carboxy-3:5-dimethylphenyl)- $\beta$ -methylglutaconic acid.

The formation of this compound proceeds as follows. The lactone ring of isodehydracetic ester undergoes fission, and simultaneously the carboxyl group is hydrolysed, with production of the dibasic acid (I),  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ ; the latter readily loses carbon dioxide (Hantzsch, A., 1883, 1083), giving the monobasic acid (II),  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}_2$ . Condensation, analogous to the formation of mesityl oxide, now occurs between the methyl group of the acetyl radicle of the acid (I) (keto-form), and the hydroxyl group of the acid (II), a molecule of water being eliminated. A second molecule of water is then lost from the enolic form of the resulting tribasic acid (III),

$\text{CH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , with production of a benzene ring. The product is a substituted  $\alpha$ -phenyl- $\beta$ -methylglutaconic acid,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , which now, owing to the tendency for the double bond to become conjugated with the phenyl group, undergoes isomerisation to

the acid,  $\text{CO}_2\text{H}\cdot\overset{\text{Me}}{\underset{\text{Me}}{\text{C}_6\text{H}_2}}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which is the

"Anschütz" acid, m. p. 234°.

This structure is clearly demonstrated by oxidising the trimethyl ester of the acid by means of ozone. Decomposition of the heavy, yellow, oily *ozonide* by means of water gives methyl acetoacetate and *dimethyl 2:6-dimethyl-1:5-terephthalonate*,

$\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ , long needles, m. p. 52°, *p*-nitrophenylhydrazone, pale yellow needles, m. p. 166°, *semicarbazone*, glistening prisms and leaflets, m. p. 183—184°. When treated in benzene solution with concentrated sulphuric acid, this ketonic ester gives a deep red coloration, which soon becomes violet. On addition of water, the benzene layer becomes carmine-red. Hydrolysis of the dimethyl ester by means of methyl-alcoholic potassium hydroxide leaves the carbomethoxyl group attached to the benzene nucleus intact. The resulting *monomethyl ester*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , has m. p. 108—109°, or + $\text{H}_2\text{O}$ , m. p. 78°, *p*-nitrophenylhydrazone, sinters at 180°; decomp. 210°. Treatment of the free acid, m. p. 234°, with ozone, and decomposition of the ozonide by means of water, give acetone, acetic acid, and 2:6-dimethylterephthalic acid; the latter is also produced if potassium permanganate is used for the oxidation. Its calcium salt crystallises with  $8\text{H}_2\text{O}$  (cf. Jannasch and Weiler, A., 1895, i, 288). The action of boiling methyl sulphate, under somewhat reduced pressure, on the sodium salt of the known methyl hydrogen dimethylterephthalate (Noyes, A., 1899, i, 284) gives the *dimethyl ester*, leaflets, m. p. 73°, b. p. 165—167°/14 mm., hydrolysis of which by means of aqueous alkali gives the isomeric monomethyl ester, 4-carbomethoxy-3:5-dimethylbenzoic acid, long needles, m. p. 154°.

In the preparation of Anschütz's acids,  $\beta\beta$ -dimethylacrylic acid and a *monoethyl ester* of the acid, m. p. 234°, are also formed (Feist

and Beyer, *loc. cit.*). The acid ester is an asbestos-like mass,  $+H_2O$ , m. p.  $175^\circ$ , and forms insoluble *ferric* (brown), *chromium* (green), *lead*, *tin*, and *silver* salts. Conversion of the tribasic acid into its trimethyl ester is most readily accomplished by heating the sodium salt with methyl sulphate under somewhat reduced pressure. The action of 3% methyl-alcoholic hydrogen chloride leads gradually to the formation of a *monomethyl* ester, which has m. p.  $171^\circ$ , but resolidifies on further heating, and then has m. p.  $228^\circ$ . By still more prolonged action of an excess of alcoholic acid, a substance, rods, m. p.  $139-140^\circ$ , presumably a *dimethyl* ester, is produced.

W. S. N.

**Experiments on the Synthesis of the Polyacetic Acids of Methane. VIII. An Improved Synthesis of Methanetri-acetic Acid.** MARCEL HENRY DREIFUSS and CHRISTOPHER KELK INGOLD (T., 1923, 123, 2964—2967).

**The Interaction of  $\beta\beta'$ -Dichlorodiethyl Sulphide, Sulphoxide, and Sulphone with Glycine Ester and with Potassium Phthalimide.** ALBERT ERIC CASHMORE and HAMILTON MCCOMBIE (T., 1923, 123, 2884—2890).

**Oxidation of Hydrocarbons to Formaldehyde.** R. SCHÖNFELDER (*Ber. Ges. Kohlentechnik*, 1923, [iv], 247—263; from *Chem. Zentr.*, 1923, [iv], 206—207).—When methane is passed with steam and air over copper or silver heated at  $500^\circ$ , 55 to 58% is oxidised to formaldehyde, 25—40% is unattacked, whilst 10—20% is burnt to carbon monoxide, carbon dioxide, and water. By the use of different catalysts, or activated carbon, or by silent electrical discharge, a certain amount of formaldehyde can always be obtained from methane and air. Better yields are obtained using unsaturated gaseous hydrocarbons.

G. W. R.

**The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. IV. Some Further Experiments on the Action of Oxygen on Ethylene.** E. W. BLAIR and T. SHERLOCK WHEELER (*J. Soc. Chem. Ind.*, 1923, 42, 415—417r).—The authors' experiments on the oxidation of ethylene (A., 1922, i, 917) have been repeated by an improved method and the former results were confirmed. The amount of interaction occurring depends more on the concentration of the interacting gases than in the case of methane; this may be due to the fact that in the ethylene experiments the reaction was less a surface effect than in the methane experiments. A large excess of oxygen, even at  $560^\circ$ , retards the oxidation so much that about 50% of the ethylene consumed appears as acetaldehyde and a further 29% as formaldehyde. The arguments for and against the view that acetaldehyde is an intermediate product in the production of formaldehyde are considered. Possibly in slow oxidations acetaldehyde is difficult to oxidise, and when it does at length oxidise it breaks down to carbon monoxide or carbon dioxide and water. The reason why formaldehyde is oxidised to formic acid rather than decomposed into carbon monoxide and hydrogen may be that

the latter process is endothermic. The ethylene  $\rightarrow$  acetaldehyde  $\rightarrow$  formaldehyde sequence is sound thermochemically.

E. H. R.

**Kinetic Investigation of the Oxidation of Acetaldehyde by Means of Hydrogen Peroxide, which can be regarded as a Partial Autoxidation Reaction.** L. REINER (*Z. anorg. Chem.*, 1923, 127, 187—204).—Pure acetaldehyde is oxidised only very slowly by hydrogen peroxide, but the reaction is autocatalysed by the acetic acid formed. It is found, however, that this explanation of the reaction by autocatalysis is not entirely satisfactory, and it is suggested that it is not the aldehyde, but rather the acetic acid, which forms a compound with the hydrogen peroxide present, and that this complex decomposes with relative slowness. H. H.

**The Grignard Synthesis of Aldehydes.** CHARLES EDMUND WOOD and MERVYN ARTHUR COMLEY (*J. Soc. Chem. Ind.*, 1923, 42, 429—432r).—The preparation of a number of aldehydes, including propaldehyde, *n*-butaldehyde, cyclohexanecarbaldehyde, phenylacetaldehyde and benzaldehyde, from Grignard compounds and ethyl orthoformate are described in detail. To obtain good yields, it is necessary to heat the reaction mixture for some time under a reflux condenser, and it does not seem possible to replace more than one ethoxyl group in the orthoformate by aryl or alkyl groups. After part of the ether has been distilled off, the product is treated with ice-water and the ethereal acetal layer is separated. The acetal is then hydrolysed with 5*N*-sulphuric or hydrochloric acid, preferably in stages, as prolonged heating of the aldehyde with acid causes polymerisation. The aldehyde is removed at the end of each stage with sodium hydrogen sulphite, and the unchanged acetal recovered and treated again with acid. In this manner, high yields of the aldehydes are obtained. A method is described by which a 54% yield of ethyl orthoformate can be obtained by adding sodium and chloroform portion-wise to boiling absolute alcohol. E. H. R.

**Action of Sodamide on the Chloro-compounds resulting from the Action of Phosphorus Pentachloride on Aldehydes and Ketones.** BOURGUEL (*Compt. rend.*, 1923, 177, 823—825).—The conversion of alkylidene dichlorides into single acetylenic hydrocarbons is difficult to effect, using alcoholic or solid potassium hydroxide. Thus,  $\beta\beta$ -dichloropentane (from methyl *n*-propyl ketone), with these reagents, affords a mixture of pentinenes boiling at 45—55°, whereas the two possible individual pentinenes boil, respectively, at 40° and 55°. Similarly,  $\beta\beta$ -dichlorohexane gives a mixture of hexinenes, b. p. 80—85°, whereas the individuals present boil at 70° and 83°, respectively. When, however, a dichloro-derivative, dissolved in toluene or xylene, and heated at 100—130°, is treated with sodamide, a 60% yield of the pure normal acetylenic hydrocarbon results.

*n*-Heptaldehyde gives with phosphorus pentachloride a mixture

of  $\alpha\alpha$ -dichloroheptane and  $\alpha$ -chloro- $\Delta^2$ -heptene, which are readily separated. Either compound, on treatment with sodamide, affords *n*-heptinene, b. p. 99–100.5°. Methyl *n*-propyl ketone, on treatment with phosphorus pentachloride, gives a mixture (separable by distillation under diminished pressure, keeping the temperature below 45°), of (1)  $\beta$ -chloro- $\Delta^2$ -pentene (b. p. 88–89°/760 mm.,  $d^{20}_4$  0.903,  $n^{20}_D$  1.421; formed, presumably, not by loss of hydrogen chloride from the dichloro-compound, but by the action of phosphorus pentachloride on the enol,  $\text{OH}\cdot\text{CPr}^2\cdot\text{CH}_2$ ) and (2)  $\beta\beta$ -dichloro-pentane, b. p. 36–37°/20 mm., or 128–129°/760 mm.,  $d^{20}_4$  1.040,  $n^{20}_D$  1.434. This substance reacts readily with sodamide, first giving the chloropentene (which reacts less readily with sodamide) and finally pure *n*-pentinene.

E. E. T.

**$\gamma$ -Hydroxyaldehydes. V. Ketocyclic Desmotropy in the Case of  $\gamma$ -Hydroxy-*n*-novadecaldehyde.** BURCKHARDT HELFERICH and HANS KÖSTER (*Ber.*, 1923, 56, [B], 2088–2094).—The term ketocyclic desmotropy is applied to the desmotropy between an open and a cyclic form, such as has been assumed in the case of the reducing sugars and established for  $\gamma$ - and  $\delta$ -hydroxyaldehydes (cf. A., 1920, i, 11; 1922, i, 431). The isolation of the individual desmotropes has not hitherto been possible. Attempts are now described to prepare crystalline compounds of this type. It is shown that a case of desmotropy between two or several forms is presented by  $\gamma$ -hydroxynonadecaldehyde; one of these, possibly one of the two cyclic racemic varieties which are possible by reason of the presence of two dissimilarly situated, asymmetric carbon atoms, has been isolated in the homogeneous condition. Also a diol has been prepared in good yield from solutions of the aldehyde the formation of which can be ascribed only to the presence of the aldehydic variety.

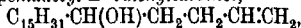
The gradual addition of palmityl chloride to a solution of ethyl sodioacetoacetate in ice-cold, absolute alcohol leads to the formation of *ethyl palmitylacetoacetate*,  $\text{COMe}\cdot\text{CH}(\text{CO}\cdot\text{C}_{15}\text{H}_{31})\cdot\text{CO}_2\text{Et}$ , m. p. 36–36.5° (the *sodio*-derivative is described). It is converted by cautious hydrolysis with water into *ethyl palmitylacetate*, m. p. 37–38° rising to m. p. 41° after long preservation; the *copper* salt,  $\text{C}_{40}\text{H}_{74}\text{O}_6\text{Cu}$ , crystallises in pale green needles, m. p. 111°. The constitution of the ester is established by its hydrolysis with aqueous sodium hydroxide solution to methyl pentadecyl ketone, m. p. 48° (semicarbazone, m. p. 127°). Ethyl palmitylacetate is transformed by phenylhydrazine hydrochloride in the presence of a few drops of concentrated hydrochloric acid at 150–160° into 1-phenyl-3-pentadecylpyrazol-5-one,  $\text{NPh}\cdot\text{N}=\text{C}\cdot\text{C}_{15}\text{H}_{31}$ , m. p. 75°,  $\text{CO}\cdot\text{CH}_2$

which gives an orange-coloured, crystalline precipitate with nitrous acid and a blue dye with ferric chloride; it is converted by methyl iodide in the presence of methyl alcohol at 100–120° into 1-phenyl-2-methyl-3-pentadecylpyrazol-5-one, needles, m. p. 66°, which yields pale green needles with nitrous acid. When free phenylhydrazine reacts with ethyl palmityl acetate, the compound (?) 4:4'-bis-

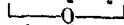
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1-phenyl-2-pentadecylpyrazol-5-one, colourless crystals, m. p. 238°, is also produced.

The introduction of the allyl group into ethyl palmitylacetate cannot be conveniently effected. On the other hand, palmityl chloride and ethyl sodioallylacetate give ethyl palmitylallylacetate which, without being completely purified, is hydrolysed by aqueous-alcoholic potassium hydroxide solution to palmityl  $\Delta^7$ -butenyl ketone,  $C_{15}H_{31}\cdot CO\cdot CH_2\cdot CH_2\cdot CH\cdot CH_2$ , m. p. 52° (semicarbazone, m. p. 80°). The ketone is converted by ozone in glacial acetic acid solution and subsequent reduction of the ozonide and peroxide with zinc dust into  $\gamma$ -keto-n-nonadecaldehyde,  $C_{15}H_{31}\cdot CO\cdot CH_2\cdot CH_2\cdot CHO$ , m. p. 60–65°; it is reduced by sodium and alcohol to pentadecyl- $\Delta^7$ -butenylcarbinol,



m. p. 50°. Ozonisation of the carbinol leads to the production of  $\gamma$ -hydroxynonadecaldehyde,  $C_{15}H_{31}\cdot CH\cdot CH_2\cdot CH_2\cdot CH(OH)$ , or



$C_{15}H_{31}\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CHO$ , which, after being purified by distillation under greatly diminished pressure (b. p. 169–173°/0.06 mm.), has m. p. 37°, rising to m. p. 48° in fourteen days;  $d_4^{20}$  0.86986,  $n_D^{20}$  1.4497. When allowed to crystallise slowly from xylene at the atmospheric temperature, it gives flattened prisms, m. p. 64°, whereas the material obtained from the mother-liquor has m. p. (indefinite) 30–40° and 40–49°. A solution of  $\gamma$ -hydroxynonadecaldehyde in ether is transformed by magnesium ethyl bromide into the corresponding diol,  $C_{21}H_{44}O_2$ , m. p. 95°, which is characterised further by conversion into the diacetate,  $C_{21}H_{44}O_4$ .  
H. W.

**Two Methyl Derivatives of Acetone[isopropylidene]Xylose.** OLAV SVANBERG (*Ber.*, 1923, 56, [B], 2195–2199).—In the preparation of xylose diisopropylidene ether, the neutralisation of the sulphuric acid used as condensing agent is conveniently effected by a slight excess of concentrated sodium hydroxide solution (cf. Freudenberg and Ivers, A., 1922, i, 523). The monoisopropylidene compound is obtained as described previously (this vol., i, 540). It is methylated by silver oxide and methyl iodide in the presence of anhydrous acetone, and the products are separated from one another by fractional distillation in a high vacuum. Monomethylisopropylidene xylose,  $C_9H_{16}O_5$ , crystallises in needles, m. p. 78°, b. p. 105–107°/0.5 mm.,  $[\alpha]_D^{20}(\text{c}_{\text{H}_2\text{O}}) -21.4^\circ$  in aqueous solution. It is converted by hydrolysis with dilute acids into a dextrorotatory sugar which has  $[\alpha]_D^{20}(\text{c}_{\text{H}_2\text{O}}) +41.95^\circ$  (equilibrium value). Dimethylisopropylidene xylose,  $C_{10}H_{18}O_5$ , is a mobile, highly refractive liquid, b. p. 78–80°/0.5 mm.,  $[\alpha]_D^{20}(\text{c}_{\text{H}_2\text{O}}) -43.3^\circ$  when dissolved in water. The corresponding dimethyl-xylose has  $[\alpha]_D^{20}(\text{c}_{\text{H}_2\text{O}}) +24^\circ$ ; it could not be caused to crystallise. When treated with phenylhydrazine in dilute acetic acid solution, it gives distinct evidence of the formation of an osazone, thus showing that the isopropylidene group of monoisopropylidene xylose is probably present in the  $\alpha\beta$ -position; unfortunately, it could only be caused to

crystallise with great difficulty, and is so readily oxidised on exposure to air that an analysis could not be made. The methylated isopropylidene xyloses are oxidised about equally readily by dilute, alkaline permanganate with disappearance of the phloroglucinol reaction and production of large quantities of oxalic acid. It is therefore probable that the primary alcoholic group in position 5 is substituted, which is necessarily the case with the dimethyl derivative. The monomethyl compound is probably  $\epsilon$ -methyl- $\alpha\beta$ -isopropylidene xylose.

H. W.

**Acetone Sugars. IV. Experiments with Galactose and Mannose.** KARL FREUDENBERG and RALPH M. HIXON (*Ber.*, 1923, 56, [B], 2119—2127; cf. Freudenberg and Doser, this vol., i, 652).—The series of reactions by which it has been shown that the hydroxyl group in position 3 is unsubstituted in the diacetone compounds [diisopropylidene ethers] of dextrose and levulose has been applied to galactose and mannose; in these cases, however, the reactions occur in a different manner, which does not throw any light on the constitution of the sugar derivatives.

Galactose is converted by acetone in the presence of hydrogen chloride or sulphuric acid (cf. Svanberg and Sjöberg, this vol., i, 540) into *diacetone galactose* [*galactose diisopropylidene ether*], a colourless, very viscous liquid, b. p. 131—139°/0.2—0.5 mm.,  $[\alpha]_{D}^{20}$  yellow  $-60.9^\circ$  when dissolved in *s*-tetrachloroethane. It is transformed by toluene-*p*-sulphonyl chloride in the presence of pyridine into *toluene-p-sulphonyl* derivative, m. p. 91—92°,  $[\alpha]_{D}^{20}$  yellow  $-64.7^\circ$  in *s*-tetrachloroethane. The compound reacts very readily with hydrazine, but the primary hydrazide could not be caused to crystallise, and gave only uninviting condensation products with benzaldehyde, *m*-nitrobenzaldehyde, piperonal, or acetone; it condenses, however, readily with phenylcarbimide to yield the *dianilide* of *diisopropylidenegalactosylhydrazinedicarboxylic acid*,  $C_{12}H_{19}O_5N(CO\cdot NHPh)\cdot NH(CO\cdot NHPh)$ , needles, m. p. 227° (decomp.). The primary hydrazine is accompanied by *as-di-diisopropylidenegalactosylhydrazine*,  $(C_{12}H_{19}O_5)_2N\cdot N\cdot NH_2$ , needles, m. p. 129—130°,  $[\alpha]_{D}^{20}$  yellow  $-77^\circ$  when dissolved in *s*-tetrachloroethane, which is oxidised by powdered potassium permanganate in the presence of anhydrous acetone to *tetradiisopropylidenegalactosyltetrazen*,

$(C_{12}H_{19}O_5)_2N\cdot N\cdot N\cdot N(C_{12}H_{19}O_5)_2$ , m. p. 103—104°,  $[\alpha]_{D}^{20}$  yellow  $-76.3^\circ$  in *s*-tetrachloroethane.

*Diacetone mannose* [*mannose diisopropylidene ether*], needles, m. p. 118°,  $[\alpha]_{D}^{20}$  yellow  $+14.3^\circ$  when dissolved in *s*-tetrachloroethane, is prepared in 84—90% yield from mannose and acetone containing 1% of hydrogen chloride. Its conversion into the toluene-*p*-sulphonyl derivative could not be satisfactorily effected. The substances react readily in the presence of pyridine, but the derivatives appear to react immediately with the solvent to form a quaternary ammonium salt. Interaction also takes place easily between sodium diacetone mannose and toluene-*p*-sulphonyl chloride in the presence of light petroleum, but the product is amorphous.

The diisopropylidene ethers of dextrose, galactose, mannose, and

lævulose are readily methylated by the action of methyl iodide on their sodium derivatives, which are readily formed when the parent compounds are treated with sodium in the presence of an indifferent solvent. They are more freely soluble than the parent sugars in light petroleum, ether, or benzene. They are decomposed by exposure to air or by sodium hydrogen carbonate. They remain as pale yellow, resinous masses when the solvent is removed. Previous to methylation, the solvent is removed under diminished pressure, and the residue is then treated with methyl iodide at 30–40°. *Diisopropylidene-methyl-galactose* is a very viscous liquid, b. p. 109–115°/0.2–0.5 mm.,  $[\alpha]_{D}^{25}$  yellow –63.2° in *s*-tetrachloroethane. *Diisopropylidene-methyl-mannose* has m. p. 37°, b. p. 118–124°/0.2–0.5 mm.,  $[\alpha]_{D}^{25}$  yellow –41.0° when dissolved in *s*-tetrachloroethane. 3-Methyl-dextrose and 3-methyl-fructose are obtained by the hydrolysis of the corresponding diacetone compounds with dilute sulphuric acid (cf. Irvine and Hogg, T., 1913, 103, 573); under similar conditions, *diisopropylidene-methyl-mannose* unexpectedly yields mannose. H. W.

**The Behaviour of the More Important Carbohydrates (Dextrose, Galactose, Lævulose, Mannose, Maltose, Lactose, Sucrose) in Strong Acid, Alkali, Sulphite, and Hydrogen Sulphite Solutions. III. The Action of Alkalis on the Carbohydrates; the Action of Sodium Sulphite on the Carbohydrates, especially on Dextrose; the Action of Sodium Hydrogen Sulphite on the Carbohydrates.** B. BLEYER and H. SCHMIDT (*Biochem. Z.*, 1923, 141, 278–296).—In the presence of alkali, dextrose, galactose, and lactose show primary and secondary rotational changes similar to those observed in acid solution (this vol., ii, 524), with the difference that increasing hydroxyl concentration shifts the equilibrium towards the  $\beta$ -form as shown by the lowering of specific rotation, whilst increasing hydrogen-ion concentration is shown to favour the  $\alpha$ -modification (*loc. cit.*). The secondary changes in rotation produced by alkali are due to isomerisation and break down of the sugar into saccharins and trioses, whereas the corresponding changes produced by acid were ascribed to the synthesis of di- and poly-saccharides. It is postulated that sugar synthesis occurs by way of the  $\alpha$ -form, and break-down through the  $\beta$ -form, with the intermediate formation of a reactive " $\gamma$ -form,"

to which the four carbon ring structure 
$$\begin{array}{c} \text{—C—CH(OH)—CH(OH)—CH(OH)—CH(OH)—} \\ | \\ \text{OH} \end{array}$$

is ascribed.

Dextrose solutions, when boiled with sodium sulphite for twenty minutes, become coloured and practically inactive, but on being neutralised the colour disappears and the solution becomes levorotatory. From the decolorised and slightly acid solution, lævulose-phenylmethylsazone (m. p. 158°) was obtained. The increasing levorotation in acid solution is due to the formation of relatively inactive bisulphite compounds by the aldehydic degradation products and by dextrose and mannose. Lævulose does not form such

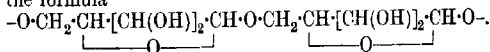
compounds, and its laevorotation therefore becomes more apparent. The author regards the aldehydic form of the reducing carbohydrates as participating in the state of equilibrium in aqueous solution, and from observations of the effect of sodium hydrogen sulphite in lowering the specific rotations of dextrose, galactose, and lactose, it is shown that this reagent displaces the equilibrium towards the aldehyde form. The behaviour of mannose in bisulphite solution is exceptional; it shows an initial laevorotation changing to a dextrorotation which is close to the normal specific equilibrium rotation in water.

J. P.

**Sources of the Rare Sugars (Melibiose).** T. SWANN HARDING (*Sugar*, 1923, 25, 514—516).—If in the method of preparing melibiose elaborated by Hudson and Harding (A., 1916, i, 120) glacial acetic acid be used for the final crystallisation in place of alcohol, the yield is improved and crystallisation occurs rapidly and certainly. After washing the sugar mass with alcohol, it is dried for twenty-four hours in a vacuum at room temperature, ground to a fine powder, and re-dried in a vacuum while the temperature is gradually raised to 120°. Previous work on the preparation of this disaccharide is reviewed.

J. P. O.

**Constitution of Polysaccharides. II. Constitution of Xylan.** S. KOMATSU, TETSUJI INOUE, and RISABURO NAKAI (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1923, 7, 25—30; cf. Heuser and Ruppel, A., 1922, i, 810).—Xylan from wheat straw was partly methylated, using methyl sulphate and sodium hydroxide, that from rice straw being methylated in the same manner, supplementing this methylation by treatment with silver oxide and methyl iodide. The dimethylxylan softened at 50—60°, and had  $[\alpha]_D^{20} +30.45^\circ$  in chloroform. Hydrolysis with 5% hydrochloric acid converted it into a dimethylxylose, which, on oxidation with dilute nitric acid, gave  $\alpha\beta$ -dimethoxyglutaric acid ( $[\alpha]_D +132^\circ$  in alcohol). The dimethylxylose is therefore the  $\beta\gamma$ -derivative and xylan must have the formula



E. E. T.

**A Sulphuric Acid Ester of Starch.** R. TAMBA (*Biochem. Z.*, 1923, 141, 274—277).—By the action on starch of a mixture of chlorosulphonic acid and chloroform in dry pyridine an amylo-disulphuric acid was obtained, which by the action of alcoholic potassium hydroxide was converted into, and isolated as, the potassium salt,  $\text{C}_6\text{H}_8\text{O}_6(\text{SO}_3)_2\text{K}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . The product had no reducing action until hydrolysed by hot acids, and did not give a blue colour with iodine after complete removal of traces of unchanged starch. It had  $[\alpha]_D^{20} +134.5^\circ$  ( $c=0.766$ ).

J. P.

**Fatty Acid Esters of Polymeric Carbohydrates.** P. KARRER and ZORKA ZEGA (*Helv. Chim. Acta*, 1923, 6, 822—826).—In a previous paper (this vol., i, 276), cellulose hexapalmitate was described. A number of other cellulose and starch esters of fatty

acids have now been prepared by the action of the fatty acid chlorides on the carbohydrates in quinoline solution. *Cellulose hexastearate*,  $C_{12}H_{14}O_{10}(CO\cdot C_{17}H_{35})_6$ , forms a slightly yellow powder with no definite melting point ( $83-118^\circ$ );  $[\alpha]_D^{18} -0.79^\circ$ . *Starch hexapalmitate*,  $C_{12}H_{14}O_{10}(CO\cdot C_{15}H_{31})_6$ , sinters at  $54^\circ$  and melts completely at  $75^\circ$ ;  $[\alpha]_D^{18} +53.54^\circ$ . *Starch hexastearate*,

$C_{12}H_{14}O_{10}(CO\cdot C_{17}H_{35})_6$ , sinters at  $69^\circ$  and is completely melted at  $86^\circ$ ;  $[\alpha]_D^{18} +49.38^\circ$ . Inulin condenses with palmityl chloride, giving an amorphous *inulin palmitate*, probably the compound,  $C_6H_7O_5(CO\cdot C_{15}H_{31})_3$ , sintering at  $45^\circ$ , m. p.  $52.5^\circ$ . *Inulin stearate* melts between  $60^\circ$  and  $63^\circ$ .

E. H. R.

**Polysaccharides. XXI. Lichenin. II.** P. KARRER, B. JOOS, and M. STAUB (*Helv. Chim. Acta*, 1923, 6, 800-816).—The close chemical similarity between lichenin and cotton cellulose has already been pointed out (this vol., i, 541). The further study of lichenin has now been facilitated by its preparation in a dry but completely soluble form. The damp lichenin obtained by extraction of Iceland moss with boiling water is soaked twice for twelve hours in 96% alcohol and then for two days in absolute ether. It is then collected on a filter and dried very slowly in a vacuum desiccator. It is thus obtained as a loose, white mass, which is easily powdered and dissolves to a clear colloidal solution in boiling water. The acetolysis of lichenin by the acetic anhydride-sulphuric acid mixture goes much more slowly than that of cotton-cellulose, either in the hot or cold, and the yield of octa-acetylcellobiose is much smaller from lichenin. The soluble lichenin is, however, much more readily attacked than the ordinary sparingly soluble form. It is not considered that the different behaviour of lichenin and cotton-cellulose denotes any essential constitutional difference; it is more probably due to different degrees of dispersity between substances having slightly different chemical constitutions. The points of resemblance between the two substances are tabulated.

The enzyme or mixture of enzymes present in the alimentary canal of the edible snail ferments soluble lichenin to dextrose completely in a few hours. Provisionally the enzyme is called snail *lichenase*. The optimum acidity for the fermentation is  $p_H$  5.2, and the reaction proceeds for about 40% of its course unimolecularly; for the rest, the substrate attacked is proportional to the square root of the time. Sparingly soluble lichenin is attacked vigorously at first, but soon the rate falls off and becomes extremely slow. Cotton-cellulose is attacked to some extent, but sparingly and incompletely on account of its insolubility. The fermentation obviously depends on the dispersity of the substrate; the unimolecular portion of the soluble lichenin fermentation probably ends with the disappearance of the most highly disperse particles. In the case of a pure lichenase, the amount of hydrolysis is proportional to the square root of the concentration of the enzyme. This relation affords a means of comparing enzyme

preparations of different strengths and of standardising the preparations.  
E. H. R.

**Lignin.** P. KARRER and B. BODDING-WIGER (*Helv. Chim. Acta*, 1923, 6, 817—822; cf. A., 1921, i, 771).—Whilst air-dried beech, fir, or oak saw-dust dissolves readily in acetyl bromide, the vacuum-dried material is much less readily attacked. The lignin derivative, which can also be obtained from lignin itself, contains from 10—18% of bromine, 26—28% of acetyl, and about 7—8% of methoxyl. The reaction with acetyl bromide may be applied to the study of the composition and genesis of peats, of which the peatified portion is unattacked. Peats from different sources gave from 19—33% of residue when treated with acetyl bromide, and the residue contained from 1.34—3.51% of methoxyl. By distilling lignin with zinc dust, a viscous oil was obtained which, on redistillation at 2 mm. pressure, gave fractions boiling between 66° and 280°. The fractions all contained methoxyl (about 3%) and other oxygen, probably contained in furan rings, up to about 8%. The oxygen content of the oil was smaller when the original distillation was carried out at a higher temperature. From some of the fractions a small quantity of crystals separated from which were obtained a *hydrocarbon*,  $(C_8H_8)_n$ , m. p. 210—212°, yellow needles with a greenish-blue fluorescence. It is probably a polynuclear aromatic compound, partly hydrogenated.  
E. H. R.

**Pentosans in Lignin.** EMIL HEUSER (*Cellulosechemie*, 1923, 4, 77—78).—Referring to the observations by Hägglund (this vol., i, 1066) of the presence of small quantities of pentosan in preparations of lignin obtained by the hydrolysis of pinewood by highly concentrated hydrochloric acid, the author points out that the quantity of residual pentosan in such preparations is very variable and frequently amounts to mere traces or even nothing. Such residues are to be regarded simply as impurities remaining from the incomplete action of the cold concentrated mineral acid, and their presence is not to be accepted as evidence in favour of a constitutional union of the lignin and pentosan groups.  
J. F. B.

**Bacterial Degradation of Lignin Acids.** HANS PRINGSHEIM and WALTER FUCHS (*Ber.*, 1923, 56, [B], 2095—2097).—The lignin acids are prepared by treatment of pine sawdust with sodium hydroxide solution (5%) under pressure; the clear filtrate is acidified with hydrochloric acid. The precipitate is washed repeatedly with water until free from chlorides; after desiccation it constitutes a pale yellow, amorphous powder which is almost insoluble in water or alcohol, but very readily soluble in ammonia. The aqueous solution of the ammonium salt is treated at 37° in the presence of ammonium sulphate, potassium phosphate, magnesium sulphate, and chalk with a bacterial culture derived from forest earth. The product of the change differs from the original material in containing up to half its weight of substances soluble in alcohol. The recovered acid, in particular the part which is

titratable by formol, which became still less after boiling for six hours, but returned to the original value after eighteen hours' boiling. The maximum diminution was obtained by warming for one hour on the water-bath. Concentrated solutions of hydrochloric and formic acids and twice normal sodium hydroxide gave similar results. The free amino-nitrogen as determined by Van Slyke's method did not always agree with that obtained by formol titration, indicating the possible presence of proline-like complexes. In addition to the peptide and diketopiperazine linkings in these condensation products, a methylene linking is also postulated on the ground of the capacity of glycine to reduce methylene-blue after solution in alkali. Alanine and aspartic acid gave results similar to those obtained with glycine. J. P.

**$\alpha$ -Oxides from Aldehydes and Carboxylic Acids. II.**  
JULIUS VON BRAUN (*Ber.*, 1923, 56, [B], 2178—2185).—In a recent communication (this vol., i, 1049), it has been shown that heptaldehyde can be converted very smoothly into *n*-amylethylene oxide. A number of cases are now cited which show that the reaction is widely applicable. The observations appear of interest, since the oxides can be isomerised to aldehydes which are otherwise very difficult to prepare and also on account of the pronounced odour of the substances, which makes them very suitable for the study of the relationship between constitution and odour.

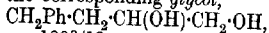
[With W. SCHIRMACHER.]—Ethyl  $\alpha$ -bromopalmitate, m. p. 27°, b. p. 224—227°/11 mm., is conveniently prepared by treating palmitic acid with bromine and phosphorus, pouring the crude brominated product into an excess of cold ethyl alcohol, and completing the esterification by warming the alcoholic solution in the presence of hydrogen chloride. It is converted by a solution of dimethylamine in benzene into ethyl  $\alpha$ -dimethylaminopalmitate,  $C_{16}H_{33}CH(NMe_2)CO_2Et$ , a viscous, almost odourless liquid, b. p. 215—217°/11 mm. (methiodide, m. p. 134°), which is reduced by sodium and alcohol to  $\beta$ -dimethylaminocetyl alcohol,

$C_{16}H_{33}CH(NMe_2)CH_2OH$ ,  
a colourless, viscous liquid, b. p. 210—213°/11 mm.; the hydrochloride is not crystalline, and the methiodide has m. p. 199—200°. The latter compound is transformed by silver oxide into the corresponding base, which decomposes when distilled in a vacuum into trimethylamine, palmitic acid (formed by oxidation of the corresponding aldehyde), and hexadecylene  $\alpha\beta$ -oxide,  $CH_3[CH_2]_{13}CH=CH_2$ ,

an almost odourless, colourless liquid, b. p. 175—180°/12 mm., m. p. 21—22°,  $d_4^{20}$  0.8457,  $n_D^{20}$  1.4445. The oxide is indifferent towards permanganate, phenylhydrazine, semicarbazide, or Schiff's solution. It appears to be isomerised readily to palmitaldehyde by treatment with acids or, to some extent, by distillation.

[With J. OSTERROTH.]— $\alpha$ -Bromo- $\gamma$ -phenyl-*n*-butyric acid is converted by ethyl alcohol and sulphuric acid into ethyl  $\alpha$ -bromo- $\gamma$ -phenyl-*n*-butyrate, a very pale yellow liquid, b. p. 157°/14 mm., which is transformed into ethyl  $\alpha$ -dimethylamino- $\gamma$ -phenyl-*n*-butyrate,

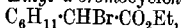
a colourless liquid, b. p.  $160^{\circ}/15$  mm. (the non-crystalline *hydrochloride* and *picrate* and the *methiodide*, m. p.  $125^{\circ}$ , are described). Reduction of the basic ester leads to the production of  $\beta$ -dimethylamino- $\delta$ -phenyl-*n*-butyl alcohol,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{NMe}_2)\cdot\text{CH}_2\cdot\text{OH}$ , a colourless liquid, b. p.  $172\text{--}173^{\circ}/22$  mm. (the *hydrochloride* and *picrate* are non-crystalline; the *methiodide* has m. p.  $155^{\circ}$ ). Distillation of the quaternary base derived from  $\beta$ -dimethylamino- $\delta$ -phenyl-*n*-butyl alcohol results in the production of trimethylamine and  $\delta$ -phenylbutylene  $\alpha\beta$ -oxide,  $\text{C}_{10}\text{H}_{12}\text{O}$ , a liquid with a very pleasant odour of roses, b. p.  $106\text{--}109^{\circ}/31$  mm.,  $d_4^{20}$  1.0029,  $n_D^{20}$  1.5129. The oxide is slowly isomerised by sulphuric acid (20%) to the corresponding aldehyde. It is converted by water at  $160\text{--}170^{\circ}$  into the corresponding *glycol*,



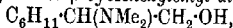
a viscous liquid, b. p.  $180^{\circ}/13$  mm., and by a solution of dimethylamine in benzene into  $\beta$ -hydroxy- $\delta$ -phenylbutyldimethylamine,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p.  $145\text{--}147^{\circ}/15$  mm. (the non-crystalline *hydrochloride* and *picrate* and the *methiodide*, m. p.  $170^{\circ}$ , are described).

[With W. MÜNCH.]—In a similar manner, *ethyl  $\alpha$ -bromo- $\gamma$ -phenoxybutyrate*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ , b. p.  $179\text{--}180^{\circ}/12$  mm., is transformed successively into *ethyl  $\alpha$ -dimethylamino- $\gamma$ -phenoxybutyrate*, a colourless liquid, b. p.  $174^{\circ}/13$  mm., and  $\beta$ -dimethylamino- $\delta$ -phenoxybutyl alcohol, a colourless, almost odourless liquid, b. p.  $186\text{--}187^{\circ}/14$  mm. The latter substance is transformed successively into the *methiodide*, m. p.  $117^{\circ}$ , and the quaternary base which, when distilled, does not yield quite homogeneous  $\delta$ -phenoxybutylene  $\alpha\beta$ -oxide.

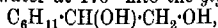
[With W. KAISER.]—*Ethyl  $\alpha$ -bromocyclohexylacetate*,



a. p.  $133\text{--}135^{\circ}/15$  mm., is transformed somewhat slowly into *ethyl  $\alpha$ -dimethylaminocyclohexylacetate*, b. p.  $123\text{--}124^{\circ}/13$  mm. (the non-crystalline *picrate* and the *hydrochloride*, m. p.  $173\text{--}174^{\circ}$  [decomp.] are described), which is remarkably smoothly reduced to  $\beta$ -dimethylamino- $\beta$ -cyclohexylethyl alcohol,



b. p.  $124\text{--}126^{\circ}/13$  mm. (the corresponding *hydrochloride* is not crystalline; the *methiodide* has m. p.  $155\text{--}156^{\circ}$ ). The quaternary base derived from the alcohol decomposes very smoothly when distilled into trimethylamine and cyclohexylethylene oxide, a colourless liquid with a very pleasant, fruity odour, b. p.  $63\text{--}65^{\circ}/14$  mm.,  $d_4^{20}$  0.9359,  $n_D^{20}$  1.4518. The oxide is remarkable for the unusual stability of the oxide ring. After agitation with sulphuric acid (20%) during twelve hours, the isomerisation to cyclohexylacetaldehyde is barely appreciable. It is transformed with difficulty by a solution of dimethylamine in benzene into  $\beta$ -dimethylamino- $\beta$ -cyclohexylethyl alcohol,  $\text{C}_6\text{H}_{11}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$  (*methiodide*, a. p.  $191^{\circ}$ ) and by water at  $170^{\circ}$  into the *glycol*,



colourless crystals, m. p.  $43^{\circ}$ , after slight previous softening, b. p. about  $150^{\circ}/13$  mm.

H. W.

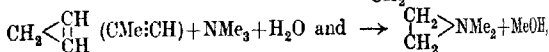
**Preparation and Chlorination of  $\alpha\beta$ -Alkylaclycarbamides.** ELWYN ROBERTS (T., 1923, 123, 2779—2782).

**Preparation and Stability of Cuprous Nitrate and Other Cuprous Salts in presence of Nitriles.** HOWARD HOULSTON MORGAN (T., 1923, 123, 2901—2907).

**The Action of Organo-magnesium Compounds on Nitriles.** **Vinylacetonitrile.** P. BRUYLANTS and J. GEVAERT (Bull. Soc. Chim. Belg., 1923, 32, 317—324).—Magnesium ethyl bromide acts with vigour on vinylacetonitrile, giving a red, granular mass, and evolving ethane copiously. After hydrolysis, five products were isolated: dipropenyl, the two geometrical isomerides of crotononitrile, and two other products. Of these  $\beta$ -methyl- $\alpha$ -ethenylglutarodinitrile has b. p. 267—270°/760 mm., 145—146°/20 mm., or 131—132°/11 mm., m. p. 13—14°,  $d_4^{20}$  0.9465 and  $n_D^{20}$  1.4594. By acid hydrolysis, this compound yields the corresponding imide, m. p. 144°, and, on acid hydrolysis, the corresponding  $\beta$ -methyl- $\alpha$ -ethenylglutaric acid, m. p. 127—128°, b. p. 203—205°/15 mm. In addition to the dinitrile (which is a dimeride of vinylacetonitrile), a liquid boiling at 215—225°/15 mm., which deposited crystals, m. p. about 150°, was isolated from the reaction mixture. Analysis showed this to be a trimeride of vinylacetonitrile. H. H.

**cycloPropene.** N. J. DENJANOV and MARIE DOJABENKO (Ber., 1923, 56, [B], 2200—2207).—The preparation of cyclopropene,  $\text{CH}_2 < \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix}$ , and its behaviour towards bromine have been investigated.

The decomposition of cyclopropyltrimethylammonium hydroxide occurs in accordance with the schemes:  $\text{CH}_2 > \text{CH} \cdot \text{NMe}_3 \cdot \text{OH} \rightarrow$



the change in the first direction being the more pronounced. The base is decomposed rapidly in a small quartz flask at about 300°; the apparatus is shielded from light and air. The gaseous product consists of cyclopropene mixed with a small proportion of allylene, from which it can be freed by treatment with ammoniacal cuprous chloride solution. cycloPropene is condensed to a colourless liquid by means of ether and solid carbon dioxide. It polymerises easily and rapidly, particularly under the direct influence of light. It readily absorbs oxygen with the formation of a pale yellow, viscous liquid. It is converted by an alcoholic solution of iodine into an unstable iodide. It unites so energetically with bromine that it must be diluted with carbon dioxide during the preparation of the bromides. Under these conditions, the crude hydrocarbon yields

a mixture of dibromocyclopropane,  $\text{CH}_2 < \begin{smallmatrix} \text{CHBr} \\ | \\ \text{CHBr} \end{smallmatrix}$ , a colourless liquid

with a sweet odour, b. p. 45°/27 mm., 135—136°/743 mm., m. p. about 0°,  $d_4^{20}$  2.1436,  $d_4^{25}$  2.1241,  $d_4^{30}$  2.1040,  $n_D^{20}$  1.5369,  $n_D^{25}$  1.5369,  $n_D^{30}$  1.5369.

bromopropene (allylene tetrabromide), b. p. 121—123°/17.5—20 mm.,  $d_4^{20}$  2.7225,  $d_4^{25}$  2.7011,  $d_4^{30}$  2.6800,  $n_D^{20}$  1.617, and *oxy-tetra-bromopropene*, b. p. 154—156°/19 mm.,  $d_4^{20}$  2.7405,  $d_4^{25}$  2.7213,  $d_4^{30}$  2.702,  $n_D^{20}$  1.6225. Dibromocyclopropane reacts very slowly with bromine in diffused light, slowly in direct sunlight. It is converted by zinc dust and alcohol into cyclopropene free from allylene.

cycloPropyldimethylamine,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{NMe}_2$ , is a colourless, mobile liquid, b. p. 59.8—60.3°/731—732 mm.,  $d_4^{20}$  0.7644,  $d_4^{25}$  0.7497,  $n_D^{20}$  1.4015. The chloroplatinate,  $\text{C}_{10}\text{H}_{24}\text{N}_2\text{PtCl}_6$ , long, orange-red needles, the picrate, long, thin leaflets, m. p. 191—192° (decomp.), the chloraurate and the methiodide, colourless crystals, are described.

H. W.

**Molecular Models: Benzene.** JARED KIRTLAND MORSE (*Physical Rev.*, 1922, 19, 243).—In a three-dimensional model of the benzene molecule, the carbon nuclei are placed at the corners of a regular octahedron and the hydrogen nuclei along its axes; three of the hydrogen nuclei are placed at a distance  $y$  and the remaining three at a distance  $z$  from their respective corners of the octahedron of edge  $x$ . Equations are given from which it is deduced that if  $x = 2.514 \times 10^{-8}$  cm. (Bragg), then  $y = 2.214 \times 10^{-8}$  cm., and  $z = 3.212 \times 10^{-8}$  cm. If the expressions given are substituted for the distinctive axes in models of naphthalene and anthracene, axial ratios in agreement with those determined crystallographically can be predicted.

A. A. E.

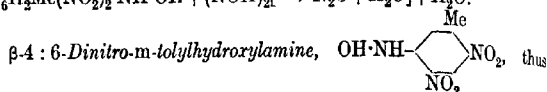
**The Formation of a Non-volatile Residue in Xylene.** P. DEKKER (*Chem. Weekblad*, 1923, 20, 575—577).—Samples of xylene subjected to several hours' boiling were found to leave a considerable residue on distillation, amounting to 5 g. per 100 c.c. after twenty-four hours' boiling. When the heating was carried out in absence of air, the non-volatile residue was still formed, although not in such large quantities; hence it is not due to oxidation. The samples were found to give strong reactions for aldehydes, to the presence of which the formation of the residue is ascribed; after shaking with strong sulphuric acid, prolonged heating produced no effect.

S. I. L.

**Action of Hydroxylamine on  $\gamma$ -Trinitrotoluene.** MICHELE GIUA (*Gazzetta*, 1923, 53, 657—660).—Borsche (this vol., i, 778) has shown that the action of hydroxylamine on ethers of nitrophenols may lead to replacement of the alkoxy-group by the hydroxylamine residue with formation of  $\beta$ -nitroaryldiethylamines. The possibility of this replacement was first pointed out by Michael and Browne (A., 1887, 663), and the action of hydroxylamine on nitro-compounds containing a labile nitro-group has been investigated by Nietzki and Dietschy (A., 1901, i, 196), Wieland and Gamberjan (A., 1906, i, 830), Angeli and Angelico (*Gazzetta*, 1901, 31, i, 27), and Meisenheimer (A., 1904, i, 150; 1906, i, 642; 1919, i, 389).

In continuation of his work on the action of bases on nitro-

derivatives containing a labile nitro-group (this vol., i, 485), the author now finds that the action of hydroxylamine on  $\gamma$ -trinitrotoluene is somewhat complex owing to the readiness with which the  $\beta$ -nitroarylhydroxylamines undergo change, and is influenced greatly by the duration of heating. In absolute alcoholic solution, the anhydrous compounds react under definite conditions in accordance with the equation:  $C_6H_2Me(NO_2)_3 + 2NH_2OH = C_6H_2Me(NO_2)_2 \cdot NH \cdot OH + (NOH)_2 \rightarrow N_2O + H_2O + H_2O$ .



obtained, forms minute, reddish-yellow crystals, m. p. 106–107° (decomp.), dyes the skin intensely yellow, gives a pale yellow solution in concentrated sulphuric acid, and yields a red coloration with either sodium hydroxide in alcoholic solution or ammonia in acetone solution. It forms an *acetyl* derivative,  $C_6H_2Me(NO_2)_2 \cdot NH \cdot OAc$ , separating in yellow crystals, m. p. 206–207° (decomp.), and when treated with acetic anhydride yields 6-nitro-3 : 4-dinitrosotoluene,  $NO_2 \cdot C_6H_2Me(NO)_2$ , which crystallises in lustrous, reddish-yellow prisms or lamellae, m. p. 209–210°.

T. H. P.

**The Sulphonation and Nitration of Naphthalene.** H. E. FIERZ-DAVID (*J. Soc. Chem. Ind.*, 1923, 42, 421–426r).—A series of investigations on the sulphonation of naphthalene has confirmed the rule established by Armstrong and Wynne that derivatives are never obtained containing sulphonic groups in the ortho-, para-, or peri-position. The disulphonic acids never contain two sulphonic groups in the same benzene nucleus. Sulphonation at temperatures below 40° with the minimum quantity of sulphuric acid to form monosulphonic acid gives a mixture containing 96% of the 1-acid and 4% of the 2-acid. The 2-acid is formed directly, not by transformation from the 1-acid. At 165°, there is formed an equilibrium mixture containing 85% of 2-acid and 15% of 1-acid. The proportion of each acid varies with the temperature, but neither can be obtained exclusively. When naphthalene is treated with just sufficient sulphuric anhydride to form disulphonic acid, below 40° there is obtained a mixture containing 70% of 1 : 5, about 25% of 1 : 6, and probably a little 2 : 7-naphthalenedisulphonic acid. The 1 : 5-disulphonic acid is readily isolated through its insoluble barium salt, which crystallises with  $1H_2O$ , not  $4H_2O$  as stated by Armstrong. Between 120° and 135°, the 1 : 5-disulphonic acid gradually disappears, in favour of the 2 : 7-acid. Above 140°, the 2 : 6-disulphonic acid appears; this also forms a sparingly soluble barium salt, but since the 1 : 5- and the 2 : 6-acids are never present together, the question of their separation does not arise. The statement that above 180° the 2 : 6-acid is the sole product is incorrect; the proportion of 2 : 6-acid probably never exceeds 30%. At 165°, taking 2 parts of 100% sulphuric acid to 1 part of naphthalene, sulphonation is complete in three hours, and the product contains 24% of 2 : 6, 10% of 1 : 6, and 65% of 2 : 7.

disulphonic acid. The anhydride of the 2:6-acid can be obtained in the pure form by heating the acid with water at 135° in a closed vessel; the other isomerides remain in solution. The free sulphonic acids generally crystallise readily and are not deliquescent.

The nitro-group never enters in the ortho-position to a sulphonic group, often in the peri- and sometimes in the meta-position. Nitration never proceeds quantitatively; as a rule 4–14% escapes nitration. Reduction of the different nitrosulphonic acids to aminosulphonic acids does not always proceed smoothly. The yield of 1:3:8-naphthylaminedisulphonic acid (ε-acid) from naphthalene-1:6-disulphonic acid, never exceeds 43%; in addition, there are formed 15% of 2:4:7-naphthylaminedisulphonic acid (Andresen acid) and 42% of unknown acids. Similarly, the yield of Cleve's acid (1:6- and 1:7-naphthylaminosulphonic acids) from naphthalene-2-sulphonic acid is never more than 65% of theory. The reduction of the nitro-2-sulphonic acids is very sensitive to acids; aminonaphtholsulphonic acids are liable to be formed.

When naphthalene-2-sulphonic acid is acted on by nitrous acid in sulphuric acid containing a trace of mercuric oxide or selenium, a new diazonium compound, probably having the constitution

$\text{OH}\cdot\text{C}_{10}\text{H}_7\begin{matrix} \diagup \text{N}_2^{(1)} \\ \diagdown \text{SO}_3^{(2)} \end{matrix}$ , is formed. This reaction has previously been observed in the anthracene series, but is new to the naphthalene series.

The author gives a list of the known salts of naphthalene- and nitronaphthalene-sulphonic acids and their solubilities as far as they are known.

E. H. R.

**The Action of Sulphur on Organic Compounds. VI.** LUDWIK SZFERL (*Roczniki Chemji*, 1923, ii, 291–313).—A short summary is given of the first five parts of the present series (*Chemik Polski*, 1917, 15, 10; 1918, 16, 111), dealing with the action of sulphur on various aromatic compounds. In the present paper, the action of sulphur on α- and β-naphthylcarbinols is described and the results are shown to be similar to those previously obtained with benzyl alcohol. Heating with small quantities of sulphur leads in each case to the production of dinaphthylcarbinyl ether, whilst the action of one molecular proportion of sulphur leads to the formation of small quantities of dinaphthastilbenes (αα and ββ, respectively), naphthaldehydes, and the corresponding acids, in addition of products containing sulphur. In the case of the β-compound, dinaphthylethane is also produced, doubtless owing to the reduction of the stilbene primarily formed.

1-Bromomethylnaphthalene was prepared by the method of Wislicenus and Elvert (*A.*, 1917, i, 202), and had m. p. 52–53° when pure; by means of potassium acetate, it was converted into α-naphthylcarbinyl acetate, a nearly colourless liquid, b. p. 172–173°/13 mm., and this was hydrolysed by means of baryta to the alcohol, m. p. 59–60° (Bamberger and Lodter, *A.*, 1888, 375). When heated with 1/100 mol. of sulphur at 160–180° for six hours, it yields water,

a very small quantity of hydrogen sulphide, and a 55% yield of *di-α-naphthylcarbinyl ether*, plates m. p. 119—120°. When heated with one molecular proportion of sulphur for ten hours at 185° and then at 200—210° for fifty hours, it gives water, hydrogen sulphide, small quantities of *α-naphthaldehyde*, *α-naphthoic acid*, and a compound of unknown constitution containing sulphur, m. p. 142.5—143.5° (*picrate*, m. p. 200—201°), in addition to traces of fluorescent material, probably *dinaphthylethylene*. When *di-α-naphthylcarbinyl ether* was heated with one molecular proportion of sulphur under similar conditions, the product contained, in addition to *α-naphthoic acid*, *s-di-α-naphthylethylene*, m. p. 161—162° (*picrate*, m. p. 210—211°), possessing a blue fluorescence in solution. The corresponding saturated compound, *s-di-α-naphthylethane*, does not possess this property; it was prepared by the action of sodium on 1-bromomethylnaphthalene in the presence of dry benzene and has m. p. 159—160° (*picrate*, m. p. 204—205°) (compare Bamberger and Lodter, *loc. cit.*).

*β-Methylnaphthalene* was converted into the *ω-bromo-compound*, m. p. 51°, and this yielded *β-naphthylcarbinyl acetate*, m. p. 51—53°, the crystalline form of which is described in detail; this was finally converted into the alcohol.

When heated with 1/100 molecular proportion of sulphur, the alcohol yields *s-di-β-naphthylethylene*, m. p. 253—254°, and *di-β-naphthylcarbinyl ether*, colourless plates, m. p. 123.5—124.5°. With one molecular proportion of sulphur, *β-naphthoic acid*, traces of *di-β-naphthylethylene*, a *hydrocarbon*,  $C_{22}H_{18}$ , m. p. 181—182° (forming a *dipicrate*, m. p. 197—198°), and a compound,  $C_{22}H_{18}S$ , m. p. 350—351°, previously obtained from *β-methylnaphthalene* and sulphur by Friedmann (A., 1916, i, 736) were obtained. The hydrocarbon,  $C_{22}H_{18}$ , is shown to be *s-di-β-naphthylethane* by its synthesis from 2-bromomethylnaphthalene and sodium; it is not fluorescent, and it is suggested that the compound to which Bamberger and Lodter assigned the above constitution (*loc. cit.*) was probably unsaturated.

No thiophen derivatives appear to be formed in the reactions studied.  
G. A. R. K.

**Attempted Preparation of Methylene-cyclopropane. Dimethylcyclopropylmethylamine.** N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1923, 56, [B], 2208—2212).—The authors have attempted to prepare methylenecyclopropane by the thermal decomposition of cyclopropylmethyltrimethylammonium hydroxide,  $\begin{matrix} CH_2 \\ | \\ CH_2 > CH \cdot CH_2 \cdot NMe_3 \cdot OH \end{matrix}$ . The amount of hydrocarbon (which consists mainly of erythrene,  $CH_2 \cdot CH \cdot CH \cdot CH_2$ ) is, however, relatively very small; the main product of the change is cyclopropylmethyl-dimethylamine.

The best yields of hydrocarbons, not exceeding 6.5%, are obtained when the base is rapidly decomposed; the gases are treated with bromine, whereby in different experiments which do not appear to proceed quite uniformly *αβγδ-tetrabromo-*n*-butane*, m. p. 117—

118°, *methylenecyclopropane dibromide*,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CBr} \cdot \text{CH}_2 \text{Br}$ , a liquid which crystallises when cooled with solid carbon dioxide, and (1)  $\alpha\beta\beta\delta$ -*tetrabromo-n-butane* are obtained.

*cycloPropylmethyldimethylamine*,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{NMe}_2$ , is a colourless, mobile, very volatile liquid, b. p. 99—99.5°/734.5 mm., 99.5—100.1°/742 mm.,  $d_4^{20}$  0.7963,  $d_4^{25}$  0.7880,  $d_4^{30}$  0.7835,  $d_4^{35}$  0.7705,  $n_D^{20}$  1.4245. The *hydrochloride*, long, very hygroscopic prisms, m. p. (indefinite) 158—160°, the *chloroplatinate*, small, orange-coloured prisms, the *chloraurate*, leaflets, the *picrate*, long yellow prisms, m. p. 103.5—104°, and the *methiodide* are described.

The cases of decomposition of quaternary ammonium hydroxides by the authors and by Willstätter and his co-workers are sufficiently numerous to allow the following generalisations to be made. (1) When the group  $\text{NMe}_3 \cdot \text{OH}$  is attached to a ring, the main product of the decomposition is the hydrocarbon, and the production of the amine is of secondary importance; (2) cyclic bases with the side chain  $\cdot \text{CH}_2 \cdot \text{NMe}_3 \cdot \text{OH}$  yield very little semicyclic hydrocarbon and much amine; (3) cyclic bases which contain the group  $\text{NMe}_3 \cdot \text{OH}$  in the side chain in such a manner that a hydrogen atom is attached to the vicinal carbon atom yield chiefly hydrocarbons containing a double bond in the side chain, the hydrogen being taken from the vicinal carbon atom.

H. W.

**Melting-point Curves of Binary Mixtures: Aniline-crotonitrile and Aniline-Vinylacetone.** FR. LAFORTUNE *Bull. Soc. chim. Belg.*, 1923, 32, 314—317.—Aniline has m. p. -6.2°, and crotonitrile, m. p. -72.1°. These compounds do not form a compound, but a eutectic at about 63% of the nitrile, with m. p. about -85°. Similarly, vinylacetone, m. p. -86.8°, does not form a compound with aniline, but a eutectic at about 4% of the nitrile, m. p. about -95°.

H. H.

**Substituted Phenylchloroamines.** KENNEDY JOSEPH REVITÉ ORTON and (the late) JOHN EDWIN BAYLISS (*T.*, 1923, 23, 2790—2792).

**The Freezing-point-Solubility Diagram of the System tetryl [Trinitrophenylmethylnitroamine]-Picric Acid.** C. TAYLOR and WILLIAM H. RINKENBACH (*Ind. Eng. Chem.*, 1923, 15, 1070—1071).—The freezing-point curves of mixtures of tetryl (m. p. 128.72°) and picric acid (121.0°) were determined. They show a discontinuity between concentrations of 44% and 3% of tetryl apparently due to the formation of a compound 1 mol. of tetryl with 1 mol. of picric acid. All these mixtures have an extreme tendency to supercool.

C. I.

**The Tenaciousness of Organic Residues. I.** JULIUS VON RAUN and KARL MOLDAENKE (*Ber.*, 1923, 56, [B], 2165—2172).—The firmness with which organic radicals are attached to carbon, nitrogen, sulphur, and arsenic has been the subject of numerous investigations. A critical review of the literature shows that the

residues cannot be arranged in any order which holds good for their relative fixity to all elements, and as different methods lead on the whole to the same arrangement of groups with regard to any one element, it follows that the experimental technique is not at fault, but that the discordance is a natural phenomenon. The main difficulty in the uniform further development of affinity series towards carbon on the one hand and the remaining elements on the other lies in the impossibility of applying the usual reagents, such as phosphorus chloride or cyanogen bromide, to the removal of aromatic residues. The difficulty can be overcome indirectly, since if two aryl residues,  $R'_{ar}$  and  $R''_{ar}$ , make a different affinity demand on an atom of carbon or nitrogen, this must be exhibited in the inverse order in the cases of the groups  $R'_{ar}CH_2-$  and  $R''_{ar}CH_2-$ . A series of experiments has therefore been undertaken on the relative firmness of the attachment of groups of the benzyl type to nitrogen, sulphur, and arsenic, and the procedure has the further advantage that it can be extended to the halogens. It is shown with regard to nitrogen that the radicles can be arranged in the series  $-C_6H_5 \cdot CH_2-$   $\alpha$ - $C_{10}H_7 \cdot CH_2-$   $\beta$ - $C_{10}H_7 \cdot CH_2 \cdot CH_2-$  and that this order is maintained with regard to bromine and chlorine. As far as the naphthalene residues are concerned, the results are in harmony with the observations of Skraup, who employed the carbinol and oxazole method, but a discrepancy exists with regard to phenyl and benzyl, which is also apparent in the hexa-arylethane series.

$\alpha$ -Naphthylmethyl chloride, long, four-sided rods, m. p.  $34^\circ$ , b. p.  $162-163^\circ/14$  mm., is prepared in relatively poor yield by the action of hydrochloric acid on  $\alpha$ -naphthylmethyl alcohol. It is more conveniently obtained by the action of phosphorus pentachloride on *benzo- $\alpha$ -naphthylmethylamide*,  $C_{10}H_7 \cdot CH_2 \cdot NHBz$  (lustrous leaflets, m. p.  $154^\circ$ ), or *benzodi- $\alpha$ -naphthylmethylamide*,  $(C_{10}H_7 \cdot CH_2)_2NBz$  (short prisms, m. p.  $134^\circ$ ). In a similar manner,  $\alpha$ -naphthylmethyl bromide, m. p.  $50^\circ$ , b. p.  $170-175^\circ/15$  mm., is readily prepared by the use of phosphorus pentabromide. *Benzo- $\beta$ -naphthylmethylamide*, short rodlets, m. p.  $144^\circ$ , and *benzodi- $\beta$ -naphthylmethylamide*, m. p.  $120-121^\circ$ , are similarly transformed into  $\beta$ -naphthylmethyl chloride, m. p.  $48^\circ$ , b. p.  $162^\circ/15$  mm., and  $\beta$ -naphthylmethyl bromide, m. p.  $56^\circ$ , b. p.  $165-169^\circ/14$  mm. The rate of hydrolysis of the halogenated compounds by hot water has been comparatively estimated.

$\alpha$ -Naphthylmethyldimethylamine,  $C_{10}H_7 \cdot CH_2 \cdot NMe_2$ , is a colourless liquid, b. p.  $148-152^\circ/16$  mm. (*hydrochloride*, m. p.  $245^\circ$ ; *picrate*, m. p.  $145^\circ$ ), which is converted by cyanogen bromide into the quaternary salt,  $(C_{10}H_7 \cdot CH_2)_2NMe_2Br$ , m. p.  $226^\circ$ , dimethylcyanamide, and  $\alpha$ -naphthylmethyl bromide. In a similar manner,  $\beta$ -naphthylmethyldimethylamine, b. p.  $130-132^\circ/14$  mm. (*hydrochloride*, m. p.  $234^\circ$ ; *picrate*, m. p.  $152^\circ$ ), is transformed by cyanogen bromide into dimethylcyanamide,  $\beta$ -naphthylmethyl bromide, and the quaternary salt,  $(C_{10}H_7 \cdot CH_2)_2NMe_2Br$ , m. p.  $217^\circ$ . The *chloroplatinate* of the corresponding quaternary chloride forms small, pale yellow crystals, m. p.  $164-166^\circ$ .

$\alpha$ -Naphthylmethyl chloride is converted by a solution of methylamine in benzene at  $100^\circ$  into a mixture of  $\alpha$ -naphthylmethylmethylamine,  $C_{10}H_7\cdot CH_2\cdot NHMe$ , b. p.  $156$ – $158^\circ/15$  mm. (hydrochloride, m. p.  $170^\circ$ ; picrate, m. p.  $206^\circ$ ), and di- $\alpha$ -naphthylmethylmethylamine,  $(C_{10}H_7\cdot CH_2)_2NMe$ , colourless rodlets, m. p.  $87$ – $88^\circ$ , b. p.  $278$ – $280^\circ/15$  mm. (hydrochloride, m. p.  $220^\circ$ ; picrate, m. p.  $166^\circ$ ).  $\beta$ -Naphthylmethylmethylamine is a liquid, b. p.  $148$ – $150^\circ/15$  mm. (hydrochloride, m. p.  $188^\circ$ ; picrate, m. p.  $105^\circ$ ), whereas di- $\beta$ -naphthylmethylmethylamine has m. p.  $87$ – $88^\circ$ , b. p.  $276$ – $278^\circ/15$  mm. (hydrochloride, m. p.  $235^\circ$ ; picrate, m. p.  $158^\circ$ ). The action of  $\beta$ -naphthylmethyl chloride on  $\alpha$ -naphthylmethylmethylamine in the presence of benzene leads to the formation of  $\alpha$ -naphthylmethyl- $\beta$ -naphthylmethylmethylamine, cubic crystals, m. p.  $145^\circ$ , b. p.  $272$ – $274^\circ/14$  mm. (hydrochloride, m. p.  $225^\circ$ ; picrate, m. p.  $159^\circ$ ). The tertiary base is decomposed by cyanogen bromide with the production of  $\alpha$ -naphthylmethyl bromide;  $\alpha$ -naphthylmethyltrimethylammonium bromide,  $C_{10}H_7\cdot CH_2\cdot NMe_3Br$ , has m. p.  $213$ – $214^\circ$ , whereas the corresponding  $\beta$ -compound has m. p.  $205$ – $206^\circ$ .

Benzyl- $\alpha$ -naphthylmethylmethylamine,  $C_{10}H_7\cdot CH_2\cdot NMe\cdot CH_2Ph$ , a pale yellow, viscous liquid, b. p.  $220$ – $222^\circ/15$  mm., is smoothly prepared from  $\alpha$ -naphthylmethyl chloride and an excess of benzylmethylamine in the presence of benzene at  $100^\circ$ ; the hydrochloride, m. p.  $218^\circ$ , and the picrate, m. p.  $219^\circ$ , are described. The base is decomposed by cyanogen bromide with production of the quaternary bromide,  $C_{10}H_7\cdot CH_2\cdot NBr$ , m. p.  $179$ – $180^\circ$ , benzyl bromide, and the cyanide,  $\alpha$ - $C_{10}H_7\cdot CH_2\cdot NMe\cdot CN$ .

H. W.

**$\alpha$ -cyclohexylcyclohexanol.** [2-Hydroxydicyclohexanol.] PIERRE BREDAS (*Compt. rend.*, 1923, 177, 958–960; cf. this vol., i, 779).—2-Hydroxydicyclohexyl (colourless liquid, b. p.  $134$ – $136^\circ/13$  mm.,  $d_{20}^{25}$  0.971,  $n_D^{25}$  1.4914; phenylurethane, prisms, m. p.  $122^\circ$ ), is formed by the interaction of magnesium cyclohexyl chloride and cyclohexene oxide, and, on oxidation with chromic acid, in acetic acid solution, affords 2-cyclohexylcyclohexanone, colourless liquid, b. p.  $128$ – $130^\circ/12$  mm.,  $d_{20}^{25}$  0.969,  $n_D^{25}$  1.4840 (semicarbazone, m. p.  $180$ – $182^\circ$ , with preliminary softening and decomposition at  $175^\circ$ ). The above alcohol is probably the *cis*-compound. The reduction of 2-cyclohexylidenecyclohexanone with sodium and alcohol (or a combination of this process with Paal-Skita reduction) affords a mixture of two stereoisomeric 2-hydroxydicyclohexyls, b. p.  $136$ – $138^\circ/13$  mm.; this mixture with phenylcarbimide gives two phenylurethanes, neither of which can be obtained in a pure state (the respective m. p. found being  $108$ – $112^\circ$  and  $122$ – $128^\circ$ ). Oxidation of the mixture of alcohols affords 2-cyclohexylcyclohexanone, identical with the ketone described above.

E. E. T.

**Phenol Solutions.** KARL GLENZ (*Helv. Chim. Acta*, 1923, 6, 826–833).—A number of properties of aqueous solutions of phenol indicate that the dissolved substance exists in two modifications. From a saturated solution, part of the phenol can be precipitated

with salt, but not from a more dilute solution. Dilution of a phenol solution diminishes its acidity more rapidly than would be expected; thus a 6.7% solution has  $p_H$  4.58 and a 1% solution  $p_H$  6.23. The acidity of a phenol solution is also reduced by warming. The percentage adsorption of phenol by charcoal is greater from a concentrated than from a dilute solution, whereas the reverse is to be expected. Addition of salt to a phenol solution increases the acidity before any salting out effect is apparent. Addition of salt to a dilute solution increases the surface tension to that of a more concentrated solution. It is concluded that concentrated solutions contain a polymerised form of phenol which is more acid than unimolecular phenol, can be salted out, is readily adsorbed, and has a higher surface tension in solution. The possibility of the existence of phenol in the keto-form,  $H_2C_6H_4O$ , is also discussed.

E. H. R.

**Derivatives of the Four Isomeric Sulphonic Acids of *m*-Tolyl Methyl Ether.** ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH (T., 1923, 123, 2982—2996).

**Reduction of *m*-Methoxybenzyl Bromide by Hydrogen Iodide.** JOHN BALDWIN SHOESMITH (T., 1923, 123, 2828—2830).

**Chloro-*o*-xlenols. I. 5-Chloro-*o*-3-xlenol, 6-Chloro-*o*-3-xlenol, and 5-Chloro-*o*-4-xlenol.** LEONARD ERIC HIXER, WILLIAM THOMAS COLLINS, and ERNEST EDWARD AYLING (T., 1923, 123, 2968—2973).

**Compounds of Antimonic Acid and Pyrocatechol.** R. WEINLAND and RUDOLF SCHOLDER (Z. anorg. Chem., 1923, 127, 343—368).—Antimony pentoxide combines with pyrocatechol to form *tripyrocatechylantimonic acid*, which is easily soluble in water, from which it crystallises in thick, yellowish-green tablets,  $SbO(O-C_6H_4OH)_3 \cdot 6H_2O$ . The salts of *potassium* ( $\frac{1}{3}H_2O$ ), *ammonium* ( $\frac{1}{3}H_2O$ ), *sodium* ( $\frac{1}{3}H_2O$ ), *silver*, *zinc* ( $8H_2O$ ), *iron* (ferrous) ( $8H_2O$ ), *nickel* ( $8H_2O$ ), *cobalt* ( $8H_2O$ ), *manganese* ( $8H_2O$ ), *copper* ( $8H_2O$ ), and *aluminium* ( $15H_2O$ ) are described. Some salts contain excess of pyrocatechol, and are regarded as co-ordination compounds of the type  $[SbO \leftarrow \begin{smallmatrix} (O-C_6H_4OH)_2 \\ O-C_6H_4O \end{smallmatrix}] \left[ M \begin{smallmatrix} C_6H_4(OH)_2 \\ 2H_2O \end{smallmatrix} \right]$ . Such are the *magnesium*, *calcium*, *barium* salts, and the similarly constituted *potassium* and *chloropenta-aquochromic* salts. In addition, a *mercuric* salt,  $[SbO(O-C_6H_4O)_2]_2Hg$ , three *pyridine* salts,  $[Sb(O-C_6H_4O)_3]H(C_5H_5N)$ ,  $[Sb(O_2C_6H_4)_3]H \cdot 2C_5H_5N$ , and  $[SbO(O_2C_6H_4)_3]H \cdot C_5H_5N \cdot H_2O$ , two *quinoline* salts,  $[Sb(O_2C_6H_4)_3]H \cdot C_8H_7N$  and  $[SbO(O_2C_6H_4)_3]H \cdot C_8H_7N$ , an anomalous *ammonium* salt,  $[Sb(O_2C_6H_4)_3]H \cdot 3NH_3$ , and a *potassium* salt,  $[Sb_2O_2(O-C_6H_4OH)_2(O_2C_6H_4)_3]K_2 \cdot 6\frac{1}{2}H_2O$ , are described.

H. H.

**Spirans. IX. Preparation and Properties of Amino- and Nitro-derivatives of Benzylidenepentaerythritol.** DAN RADULESCU and I. TANASESCU (*Bul. Soc. Ştiinţe Cluj*, 1922, i, 192—200; from *Chem. Zentr.*, 1923, iii, 138—139; cf. this vol., i, 1211).—

Benzylidenepentaerythritol,  $\text{CHPh} \begin{smallmatrix} \text{O-CH}_2 \\ \text{O-CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2\text{O} \\ \text{CH}_2\text{O} \end{smallmatrix} \text{CHPh}$ ,

shows molecular asymmetry, although it has no asymmetric carbon atom. It cannot be resolved by physical methods. Certain derivatives were accordingly prepared. *Di-o-nitrobenzylidenepentaerythritolspiran*,  $\text{C}_{16}\text{H}_{14}\text{O}_8\text{N}_2$ , is obtained from benzylidenepentaerythritol and *o*-nitrobenzaldehyde. It forms needles with m. p.  $166^\circ$ . *Di-m-nitrobenzylidenepentaerythritolspiran* is a yellow, crystalline substance, m. p.  $188$ — $189^\circ$ . *Di-p-nitrobenzylidenepentaerythritolspiran* forms needles, m. p.  $236$ — $237^\circ$ . *Di-p-dimethylaminobenzylidenepentaerythritolspiran*, from pentaerythritol and *p*-dimethylaminobenzaldehyde, forms leaflets, m. p.  $223^\circ$ . The *picrate* and the *chloroplatinate* are microcrystalline. The *o*-nitro-compound above-mentioned gives with phenylhydrazine, *o*-aminobenzaldehydephenylhydrazone,  $\text{C}_{13}\text{H}_{13}\text{N}_3$ , greenish-yellow crystals. *Di-m-aminobenzylidenepentaerythritolspiran*,  $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_2$ , is obtained by reduction of the corresponding nitro-spiran. It is a yellow, crystalline substance, m. p.  $225^\circ$ . *Di-o-aminobenzylidenepentaerythritolspiran* is an amorphous, yellow substance, m. p.  $164^\circ$ ; the *hydrochloride* has m. p.  $172^\circ$ . G. W. R.

**Kakishibu. I. Constitution of Shibuol. I.** SHIGERU KOMATSU and NAOHICO MATSUNAMI (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1923, 7, 15—23).—Kakishibu, the pale yellow, cloudy extract of unripe kaki fruit, contains a phenolic substance,  $\text{C}_{14}\text{H}_{20}\text{O}_9$ , probably a phlobatannin, for which the name *shibuol* is proposed. Shibuol (1—2%) may be obtained from kakishibu by precipitation either with a mixture of alcohol and ether, or with acetic acid, or with concentrated hydrochloric acid or with basic lead acetate. It is converted, when fused with potassium hydroxide, into gallic acid, phloroglucinol (49.7%) and a substance,  $\text{C}_{12}\text{H}_8\text{O}_5$ .

*Kakigoma*,  $\text{C}_{11}\text{H}_8\text{O}_5$ , a brown, amorphous substance obtained from the pulp of the dried fruit *dojo-hatiya*, after purification by extraction with sulphuric acid, is soluble in alkalis, insoluble in organic solvents, and, on fusing with potassium hydroxide, gives phloroglucinol (17.88%), gallic acid, and a substance,  $\text{C}_{13}\text{H}_8\text{O}_5$ . E. E. T.

**Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. VII. Aldehydes.** JULIUS VON BRAUN and FRED KOCHENDORFER (*Ber.*, 1923, 56, [B], 2172—2178).—The catalytic reduction of aldehydes under pressure has been examined in the hope of elucidating the constitution and mode of formation of some of the compounds of unexpectedly high boiling point which have been encountered previously by other workers in experiments on catalytic hydrogenation by various methods. Under the experimental conditions adopted, it is found that acetones are converted smoothly into the corresponding secondary

alcohols, and aromatic aldehydes into the primary alcohols. When, however, the aldehydic group is present in an aliphatic chain, there are obtained, in addition to the primary alcohols, secondary alcohols which arise from the doubling of the aldehyde carbon chain. Their formation is ascribed to the condensation of enolised with unchanged aldehyde,  $\text{CHR:CH:OH} + \text{H-CO-CH}_2\text{R} \rightarrow \text{CHR:CH-CO-CH}_2\text{R}$ , and subsequent reduction of the unsaturated ketone thus produced. The hypothesis is in harmony with the observation that similar effects are not produced with aromatic aldehydes or ketones.

Styryl methyl ketone is almost quantitatively reduced to  $\gamma$ -hydroxy- $\alpha$ -phenylbutane,  $\text{CH}_2\text{Ph-CH}_2\text{-CHMe-OH}$ , b. p. 117–121°/12 mm. With acetophenone, on the other hand, complete hydrogenation cannot be effected, and the product consists of a mixture of unchanged ketone and phenylmethylcarbinol. Benzaldehyde is hydrogenated rapidly and completely to benzyl alcohol. Similarly, *o*-aminobenzaldehyde dissolved in decahydronaphthalene gives *o*-aminobenzyl alcohol, m. p. 82°, in 80% yield. Cinnamaldehyde is converted into a mixture of phenylpropyl alcohol and  $\gamma$ -hydroxy- $\alpha$ -*di*-phenylhexane,  $\text{CH}_2\text{Ph-CH}_2\text{-CH(OH)-CH}_2\text{-CH}_2\text{-CH}_2\text{-Ph}$ , a colourless liquid, b. p. 224–227°/9 mm. The latter compound is converted by sodium acetate and acetic anhydride into the corresponding *acetate*,  $\text{C}_{20}\text{H}_{24}\text{O}_2$ , a colourless liquid, b. p. 225–230°/18 mm.; by phosphorus chloride into the *chloride*,  $\text{C}_{18}\text{H}_{21}\text{Cl}$ , a liquid, b. p. 215–217°/10 mm.; by chromic acid in the presence of glacial acetic acid into the *compound*,  $\text{C}_{18}\text{H}_{20}\text{O}$ , a pale yellow liquid, b. p. 214–218°/12 mm., which does not give crystalline condensation products with hydroxylamine or semicarbazide, and by zinc chloride into the saturated *hydrocarbon*,  $\text{C}_{18}\text{H}_{20}$ , a colourless liquid, b. p. 204–208°/14 mm.,  $d_4^{20}$  1.028,  $n_D^{20}$  1.5770; the latter compound is identified as 1- $\beta$ -phenylethyl-1:2:3:4-tetrahydronaphthalene,  $\text{C}_{18}\text{H}_{20}$   $\begin{matrix} \text{CH}_2 & \text{---} & \text{CH}_2 \\ & \diagdown & \diagup \\ & \text{CH}(\text{CH}_2\text{-CH}_2\text{Ph})\text{-CH}_2 \end{matrix}$ , since it is converted by lead oxide at 620–650° into naphthalene and styrene contaminated with a little ethylbenzene. The behaviour of hydrocinnamaldehyde is similar to that of cinnamaldehyde.

Phenylacetaldehyde is hydrogenated to a mixture of phenylethyl alcohol and  $\beta$ -hydroxy- $\alpha$ -*di*-phenyl-*n*-butane,  $\text{CH}_2\text{Ph-CH(OH)-CH}_2\text{-CH}_2\text{Ph}$ , colourless crystals, m. p. 41°, b. p. 204–208°/10 mm. The latter compound is converted into the corresponding *acetate*, a liquid, b. p. about 200°/17 mm., the *chloride*, b. p. 192–193°/15 mm., and the *ketone*, which could not be isolated in the completely homogeneous condition. It is converted by zinc chloride or by 2*N*-sulphuric acid at 260–280° into the unsaturated *hydrocarbon*,  $\text{C}_{16}\text{H}_{18}$ , b. p. 172–173°/9 mm.,  $d_4^{20}$  1.044,  $n_D^{20}$  1.5944, which possibly contains small amounts of 1-benzylhydrindene in addition to  $\alpha\delta$ -diphenyl- $\Delta^4$ - or - $\Delta^5$ -butene.

Heptaldehyde is hydrogenated at 140–150° to a mixture of heptyl alcohol and *heptylcarbinol*,  $\text{C}_6\text{H}_{13}\text{-CH(OH)-C}_2\text{H}_5$ , an almost odourless, fairly mobile liquid, b. p. 153–155°/9 mm. (the

corresponding *acetate*, b. p. 152—155°/14 mm., and the *chloride*, b. p. 150—155°/15 mm. are described).

Dipropenyl glycol does not combine with more than four atomic proportions of hydrogen even at 200° and is thereby converted into a mixture of the stereoisomeric octane- $\delta$ -diols. The possibility that the glycols are intermediate products in the formation of the secondary alcohols described above appears therefore to be invalidated.

H. W.

**The Catalytic Reduction of some Nitriles.** H. RUPE and E. HOEDEL (*Helv. Chim. Acta*, 1923, 6, 865—880; cf. Rupe and Glenz, this vol., i, 100).—Experiments on the reduction of benzonitrile and phenylacetoneitrile (benzyl cyanide) with hydrogen in presence of nickel have elucidated the mechanism of the reaction. The reductions were carried out in cold aqueous alcoholic solution in presence of acetic acid and a large proportion of nickel catalyst, about twice the weight of the nitrile. The first product of the reaction is the aldimine,  $\text{CHR}\cdot\text{NH}$ , part of which is reduced further to the primary amine,  $\text{CH}_2\text{R}\cdot\text{NH}_2$ . Part of the aldimine, however, is hydrolysed to aldehyde and ammonia, and the former condenses with the primary amine to form the Schiff's base,  $\text{CHR}\cdot\text{N}\cdot\text{CH}_2\text{R}$ , which is then reduced to secondary amine. The relative proportions of primary and secondary base formed depend on the ease with which the aldimine is hydrolysed into aldehyde and ammonia. When the reaction is carried out in presence of phenylhydrazine, more primary base is formed, since the aldehyde condenses preferentially with the phenylhydrazine to form a phenylhydrazone, which is itself reduced to some extent to primary base and aniline. When 25 g. of benzonitrile were reduced there were formed 3.2 g. of benzaldehyde, 4.6 g. of benzylamine, and 11.8 g. of dibenzylamine. In presence of phenylhydrazine, the products were 6.8 g. of benzaldehyde (from the phenylhydrazone), 8.8 g. of benzylamine, 1.5 g. of dibenzylamine, and 9.1 g. of aniline. Phenylhydrazine itself was found to be reduced rapidly to aniline and ammonia. Benzylideneaniline is reduced rapidly to benzyaniline. By the reduction of 40 g. of benzyl cyanide, 4.8 g. of  $\beta$ -phenylethylamine, and 27.2 g. of di- $\beta$ -phenylethylamine were obtained, whereas in presence of phenylhydrazine there were formed 5.8 g. of primary and 2.4 g. of secondary amine from 20 g. of the nitrile. Benzylidenehexylamine was readily reduced to benzylhexylamine, whereas phenylethylphenylethylideneamine, from phenylacetaldehyde and phenylethylamine, gave but a poor yield of secondary amine on account of the instability of the Schiff's base.

E. H. R.

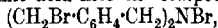
**Syntheses in the Fatty-aromatic Series. XIV. Homo-*o*-xylylene Bromide.** JULIUS VON BRAUN and FRIEDRICH ZOBEL (*Ber.*, 1923, 56, [B], 2142—2152; cf. A., 1916, i, 470).—The projected course of the preparation of homo-*o*-xylylene bromide is indicated by the scheme:  $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2 \rightarrow$   
 $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{Br} \rightarrow$   
 $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN} \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow$   
 $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{R}' \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} \rightarrow$   
 $\text{CH}_2\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ . Complete success is achieved when R

is the ethyl, but not the methyl or phenyl, group. The tendency towards ring formation is greater with homo-*o*-xylylene bromide than with xylylene bromide; numerous examples of its conversion into cyclic compounds are cited.

$\omega$ -Ethoxy-*o*-toluonitrile, b. p. 122°/12 mm., is readily obtained in almost theoretical yield by the action of alcoholic sodium ethoxide on *o*-cyanobenzyl bromide. It is easily reduced in decalhydronaphthalene solution at 130° to a mixture of the corresponding primary and secondary bases, which are smoothly separable by fractional distillation. *o*-Ethoxymethylbenzylamine,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$  (yield 40–52%), is a colourless liquid, b. p. 130°/12 mm. (*hydrochloride*, leaflets, m. p. 152°; *picrate*, needles, m. p. 148°). *Bis-o*-ethoxymethylbenzylamine,

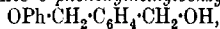


is a reddish-yellow, viscous liquid, b. p. 237°/12 mm.; the *picrate* has m. p. 93°. The non-crystalline *benzoyl* derivative is converted by fuming hydrobromic acid into the compound,



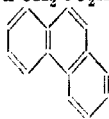
a colourless, crystalline powder, m. p. 124°, in which the bromine atom is very mobile.

*o*-Phenoxymethylbenzylamine is converted by nitrous acid in acetic acid solution into *o*-phenoxymethylbenzyl alcohol,



a colourless, crystalline mass, m. p. 50°, b. p. 216°/15 mm. The replacement of the hydroxy-group of the compound by bromine without loss of the phenyl radicle is a matter of difficulty, but can be effected by cautious treatment of it with phosphorus tribromide in the presence of chloroform, whereby *o*-phenoxymethylbenzyl bromide, colourless crystals, m. p. 54°, is produced. This compound is converted by aqueous-alcoholic potassium cyanide solution into  $\omega$ -phenoxy-*o*-tolylacetonitrile, m. p. 78°, b. p. 220°/17 mm., which is hydrolysed in alkaline solution to  $\omega$ -phenoxy-*o*-tolylacetic acid, m. p. 105°. Ethyl  $\omega$ -phenoxy-*o*-tolylacetate, b. p. 225°/15 mm., is prepared from the acid by means of ethyl alcohol and sulphuric acid; it is reduced by sodium and alcohol to  $\beta$ -*o*-tolylethyl alcohol, b. p. 120°/15 mm., the phenoxy-group being replaced by hydrogen during the reaction.

[With O. KÜHN.]—Sodium  $\omega$ -phenoxy-*o*-tolylacetate, lustrous leaflets, condenses with *o*-nitrobenzaldehyde in the presence of



acetic anhydride to give the substance,  $\text{OPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CO}_2\text{H}$ , small, pale yellow crystals, m. p. 152–153°, which is smoothly reduced by ferrous hydroxide and ammonia to the corresponding amino-acid, colourless or yellow crystals, m. p. (for either form) 142° after softening at 138°. The latter acid is transformed by successive treatment with nitrous acid and copper powder into phenoxymethylphenanthrenecarboxylic acid (annexed formula), pale yellow prisms, m. p. 201°.

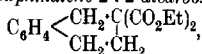
*o*-Ethoxymethylbenzylamine is converted successively into *o*-ethoxymethylbenzyl alcohol, a colourless liquid, b. p. 146°/16 mm.;

*o*-ethoxymethylbenzyl bromide, a colourless liquid which could not be caused to crystallise, b. p. 135–137°/16 mm.; *ω*-ethoxy-*o*-tolyl-acetonitrile, b. p. 150°/16 mm.; *ω*-ethoxy-*o*-tolylacetic acid, a colourless, very viscous liquid, b. p. 190°/16 mm., and ethyl *ω*-ethoxy-*o*-tolylacetate, b. p. 156°/17 mm. Partial replacement of the ethoxyl group by hydrogen occurs during the reduction of the ester by sodium and alcohol, but the main product of the change is *β*-*o*-ethoxymethylphenylethyl alcohol,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , an almost odourless liquid, b. p. 149–152°/12 mm. The alcohol is converted by protracted treatment with fuming hydrobromic acid at 100° into *o*-homoxilylene bromide, long needles, m. p. 53°, b. p. 168°/10 mm., the yield being 60% of that theoretically possible.

isoChroman,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\cdot\text{O} \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$ , b. p. 90°/12 mm., is normally

formed as by-product during the reaction, but can be made the main product if the duration is sufficiently shortened; its constitution is deduced from its analysis and the absence of a hydroxyl group, from its conversion into *o*-homoxilylene bromide by fuming hydrobromic acid, and its formation from the bromide by the action of water, or, preferably, of dilute potassium carbonate solution. *o*-Homoxilylene bromide is converted by potassium sulphide in aqueous-alcoholic solution into thioisochroman,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\cdot\text{S} \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$ , b. p. 128–130°/13 mm., which could not be obtained quite free from the corresponding oxygen compound; the additive compound with mercuric chloride,  $\text{C}_6\text{H}_4\text{S}\cdot\text{HgCl}_2$ , a colourless powder, m. p. 201°, and the methiodide,  $\text{C}_{10}\text{H}_{13}\text{IS}$ , colourless leaflets, m. p. 123°, are described.

Ethyl sodiomalonate and *o*-homoxilylene bromide give ethyl 1:2:3:4-tetrahydronaphthalene-2:2-dicarboxylate,



a colourless, odourless liquid, b. p. 180°/13 mm., which is hydrolysed to 1:2:3:4-tetrahydronaphthalene-2:2-dicarboxylic acid, a colourless, crystalline powder, m. p. 176° (decomp.); the acid is transformed by loss of carbon dioxide into 1:2:3:4-tetrahydronaphthalene-2-carboxylic acid, m. p. 97–98°.

*o*-Homoxilylene bromide is converted by a solution of dimethylamine in benzene into the very hygroscopic *N*-dimethyltetrahydroisquinolinium bromide,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\cdot\text{NMe}_2\text{Br} \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$ , which is identified by

conversion through the chloride into the previously described chloroplatinate, m. p. 230°.

*β*-*o*-Tolylethyl bromide, a colourless liquid, b. p. 112–115°/16 mm., is prepared by the action of fuming hydrobromic acid on *β*-*o*-tolylethyl alcohol at 120°; it is readily converted by bromine at 125–130° into a mixture of dibrominated substances including *o*-homoxilylene bromide, but the preparation of the latter in this manner does not appear to be practicable.

*N*-Phenyltetrahydroisquinoline, a colourless, odourless liquid,

b. p. 198°/16 mm., is prepared in almost quantitative yield by the action of an excess of aniline on *o*-homoxylene bromide; the non-crystalline *hydrochloride*, the *chloroplatinate*, and the *picrate*, yellow leaflets, m. p. 120°, are described. H. W.

**The Catalytic Reduction of  $\alpha$ - and  $\beta$ -Naphthonitrile.** H. RUPE and F. BECHERER (*Helv. Chim. Acta*, 1923, 6, 880—892).—The catalytic reduction of the naphthonitriles follows the same general course as that of other nitriles (this vol., i, 1199). At the normal dilution (30 g. in 370 c.c. of mixed solvent), the products obtained from 30 g. of  $\alpha$ -naphthonitrile were 4.5 g. of  $\alpha$ -naphthaldehyde, 1.2 g. of  $\alpha$ -naphthylmethylamine, and 15 g. of di- $\alpha$ -naphthylmethylamine.  $\alpha$ -Naphthylmethylamine is a pale yellow oil which fumes in air, b. p. 162—164°, at 12 mm.; its *hydrochloride* forms colourless leaflets. Di- $\alpha$ -naphthylmethylamine forms yellow, spherical crystal aggregates, m. p. 62°, decomposing when distilled. Its salts are very sparingly soluble, and the nitrate can be used for the gravimetric estimation of nitric acid (cf. this vol., ii, 577). When the reduction is carried out at about twice the above dilution, naphthaldehyde is not formed, but a considerable quantity of  $\alpha$ -naphthylcarbinol is obtained. The reduction of  $\beta$ -naphthonitrile does not go to completion, only about 70% of the theoretical quantity of hydrogen being absorbed. The cause of this was found to be the sparing solubility of the Schiff's base formed by condensation of  $\beta$ -naphthaldehyde with the primary amine; the Schiff's base was precipitated from solution and escaped further reduction. The products of reduction of 50 g. of  $\beta$ -naphthonitrile were 5.4 g. of di- $\beta$ -naphthylmethylamine, 25.0 g. of Schiff's base, and 7.5 g. of  $\beta$ -naphthylcarbinol.  $\beta$ -Naphthylmethyl- $\beta$ -naphthylideneamine,  $C_{10}H_7\cdot CH\cdot N\cdot CH_2\cdot C_{10}H_7$ , crystallises in lustrous scales, m. p. 175°. Di- $\beta$ -naphthylmethylamine crystallises in spherical aggregates of needles, m. p. 80°. Its salts are very sparingly soluble. E. H. R.

**Action of Heat on the Acids obtained from French and American Resins by Crystallisation.** E. KNECHT (*J. Soc. Dyers and Col.*, 1923, 39, 338—340).—The author's previous conclusion that resin consists mainly of anhydrides (Knecht and Hibbert, A., 1919, i, 338) of the formula  $(C_{20}H_{22}O_2)_2O$  is defended and additional evidence adduced in favour of this contention. *l*- and *d*-Acids of m. p. 161° obtained from the resins by repeated recrystallisation and further purification were heated in a current of carbon dioxide. The presence of water in the cool parts of the tube was evident when the temperature had reached 145°, and about half of both *d*- and *l*-acids was found to have melted. The indefinite melting points of resin acids is therefore ascribed to the formation of anhydrides. H. C. R.

**Higher Terpene Compounds. XIII. The Effect of Higher Temperatures on the Pine Resin Acids.** L. RUZICKA and H. SCHNITZ (*Helv. Chim. Acta*, 1923, 6, 833—846).—The statement of Knecht and Hibbert that when resin acids from American and French resins are heated for some hours at 180° in a current of

carbon dioxide they are converted into anhydrides (A., 1919, i, 338) does not accord with the observation of Ruzicka and Meyer that by distillation of colophony, involving heating at 250–260° for four hours, the resin acids themselves are obtained with no trace of anhydride (A., 1922, i, 547). Repetition of Knecht and Hibbert's experiment with pure abietic acid showed that no anhydride formation occurred. When abietic acid was heated at 300° for eight hours, decomposition took place, resulting in the formation of 0.28 mol. of water, 0.21 mol. of carbon dioxide, 0.06 mol. of carbon monoxide, 0.05 mol. of methane, and 0.02 mol. of hydrogen per mol. of abietic acid. The residue consisted of hydrocarbons and a mixture of acidic substances evidently formed by loss of hydrogen or of methane from abietic acid. The hydrocarbons were a mixture of abietene,  $C_{19}H_{30}$ , and abietin,  $C_{19}H_{28}$ . In all probability, anhydride formation takes place to some extent when abietic acid is heated above 250°. The anhydride cannot be distilled, but decomposes according to the equation  $(C_{19}H_{28}CO)_2O \rightarrow C_{19}H_{28} + C_{19}H_{30} + CO + CO_2$ . This is by no means the only reaction occurring, for the quantity of abietene formed exceeds the abietin, as it does in the distillation of American colophony. The decomposition of *d*-pimaric acid, from French colophony, when heated at 300°, appears to take a similar course, but the products have not been identified.

E. H. R.

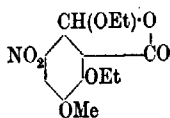
**Iodo-derivatives of *p*-Hydroxybenzoic Acid.** P. BRENANS and C. PROST (*Compt. rend.*, 1923, 177, 768–770).—3-Iodo-4-hydroxybenzoic acid (m. p. 173°, decomposing at about 200°), was prepared from 3-amino-4-hydroxybenzoic acid. The new acid forms an *acetyl* derivative, m. p. 172°, and is converted by a mixture of ethyl alcohol and sulphuric acid into the *ethyl* ester (m. p. 117°) soluble in sodium carbonate and decomposing barium carbonate. 3:5-Di-iodo-4-hydroxybenzoic acid (subliming and decomposing at 230° without melting) was obtained by the action of iodine, in presence of alcohol and mercuric oxide on the above iodo-acid or on *p*-hydroxybenzoic acid, a little 2:4:6-tri-iodophenol also being produced. The di-iodo-acid forms an *acetyl* derivative, n. p. 225°, and is converted by alcohol and sulphuric acid into the *ethyl* ester, m. p. 123°, which decomposes barium carbonate and dissolves in aqueous sodium carbonate.

E. E. T.

**Derivatives of Nitro-opianic Acid.** RUDOLF WEGSCHEIDER and NOE L. MÜLLER (*Annalen*, 1923, 433, 33–48).—The action of acetyl nitrate on opianic acid in cold acetic anhydride solution gives nitro-opianic anhydride, *nitro-opianic acid nitrate*, small, colourless, glistening, prismatic needles, m. p. 108–109°, and nitro-opianic acid acetate. The action of boiling methyl alcohol on the nitrate, or of boiling methyl-alcoholic hydrogen chloride on the acetate, gives methyl *ψ*-nitro-opianate. The acetate is also formed by heating opianic acid (4 parts), sodium acetate (4 parts), and acetic anhydride (10 parts) (Leibermann and Kleemann, A., 887, 47), but if the following proportions are taken, 2 parts, 3 parts, and 10 parts, respectively, and the mixture is heated at 75° for six hours, the product is an intensely yellow *sodium* salt,

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which explodes on heating. This has probably a quinonoid structure; it is converted by means of glacial acetic acid or hydrochloric acid into *nitromethylnoropianic acid acetate*, small, iridescent leaflets, m. p. 204–205°, the yellow *silver* salt of which is converted by contact with cold methyl iodide into *nitro-opianic acid acetate*. Nitromethylnoropianic acid reacts with boiling acetyl chloride to give *acetylnitromethylnoropianic acid acetate*, glistening leaflets (monoclinic, von Lang), m. p. 145–146°, the reverse change being effected by the action of boiling 0.1N-potassium hydroxide solution. This acetate is converted by boiling with water into nitromethylnoropianic acid acetate. Methyl *n*-nitro-opianate diacetate (monoclinic, von Lang) (Wegscheider and Müller, A., 1908, i, 896) is converted by the action of warm ethyl-alcoholic hydrogen chloride, or of warm benzene-alcoholic sodium ethoxide, into ethyl  $\psi$ -nitro-



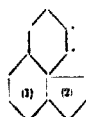
opianate. The latter, which need not be isolated, is converted by means of an excess of sodium ethoxide into the  $\psi$ -ethyl ester (annexed formula) (short, white needles, m. p. 87–89°) of 6-nitro-4-methoxy-3-ethoxyphthalaldehyde, m. p. 174–175° ( $\psi$ -methyl ester, felted white needles, m. p. 123°). The  $\psi$ -ethyl ester is obtained from the acid by boiling it with ethyl-alcoholic hydrogen chloride. The aldehydic acid is converted by the action of boiling, fuming hydrochloric acid into nitromethylnoropianic acid; the reverse change is brought about by keeping the pale sulphur-yellow *silver* salt of nitromethylnoropianic acid in contact with ethyl-alcoholic ethyl iodide, but if a benzene solution of methyl iodide is used, the product is *methyl n-nitromethylnoropianate*, glistening, yellow needles, m. p. 136–139°. The corresponding  $\psi$ -methyl ester, large, colourless tablets, m. p. 177–178°, is obtained by keeping a methyl-alcoholic solution of the acid, saturated with hydrogen chloride. The egg-yellow *potassium*, scarlet *dipotassium*, and greenish-yellow, explosive *disilver* salts of nitromethylnoropianic acid are described.

W. S. N.

**Ring-chain Tautomerism. VIII. The Effect of the cyclo-Hexane Nucleus on the Carbon Tetrahedral Angle.** ERIC WILLIAM LANFEAR and JOCELYN FIELD THORPE (T., 1923, 123, 2865–2870).

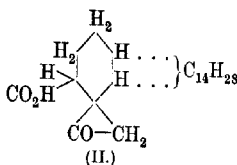
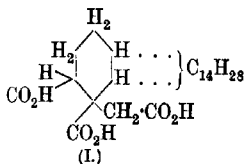
**Succinylfiorescein and its Derivatives.** SIDNEY BIGGS and FRANK GEO. POPE (T., 1923, 123, 2934–2943).

**The Number of Atoms in Ring II of the Molecules of Cholesterol and Bile Acids.** A. WINDAUS, A. ROSENBAUGH, and TH. RIEMANN (Z. physiol. Chem., 1923, 130, 113–125).—Ring

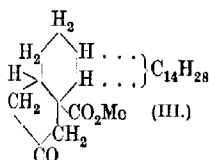


(2) of the cholesterol molecule (annexed skeleton formulæ) may contain five or six carbon atoms. By successive oxidation of cholesterol a tribasic acid,  $C_{26}H_{42}O_6$ , is obtained, and this acid loses a molecule of carbon dioxide and one of water to form the monobasic acid,  $C_{24}H_{40}O_3$ , of which (III) represents the methyl ester. This acid on oxidation yields a tribasic acid,  $C_{24}H_{40}O_6$  (Windaus, A., 1912, i, 449), which,

assuming a five-membered ring, would have the formula (I). When this tribasic acid is heated at  $215^{\circ}$  for thirty minutes, a ketonic acid,  $C_{23}H_{38}O_3$ , is formed, and when this ketonic acid is oxidised a tribasic acid,  $C_{23}H_{38}O_6$ , m. p.  $180-185^{\circ}$ , is obtained (*trimethyl ester*, needles, m. p.  $74^{\circ}$ ). This acid loses carbon dioxide when boiled in acetic acid containing hydrochloric acid; it is therefore a derivative of malonic acid. If ring II in cholesterol were six-membered it would not be possible for this substance to be a malonic acid derivative. The acid formed on heating the acid  $C_{23}H_{38}O_6$  has the formula  $C_{22}H_{38}O_4$ , needles, m. p.  $210^{\circ}$  (*anhydride*, leaflets, m. p.  $124^{\circ}$ ). The monobasic acid,  $C_{24}H_{40}O_3$ , forms a *methyl ester*, needles, m. p.  $65^{\circ}$ , difficult to hydrolyse, and the monobasic acid,  $C_{23}H_{38}O_3$ , also forms a *methyl ester*, prisms, m. p.  $70^{\circ}$ , but this is easily hydrolysed. From this fact it is considered that formula



(II) represents the most probable constitution of the acid  $C_{23}H_{38}O_3$ . This is confirmed by the fact that oxidation of the *methyl ester* of

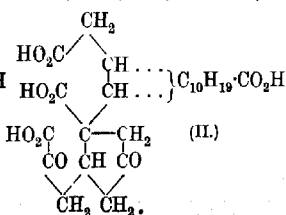
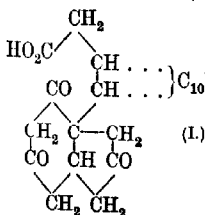


the acid  $C_{24}H_{40}O_3$ , which has the formula (III), needles, m. p.  $65^{\circ}$ , results in formation of the *monomethyl ester* of the tri-carboxylic acid  $C_{24}H_{40}O_6$ , m. p.  $189^{\circ}$ , which on distillation in a high vacuum yields the acid,  $C_{23}H_{38}O_3$ , itself (*semicarbazone*, m. p.  $226^{\circ}$ ). The acid  $C_{24}H_{40}O_3$ , m. p.  $147^{\circ}$ , when dissolved in acetic acid and treated with zinc amalgam and hydro-

chloric acid, is reduced to form an acid,  $C_{24}H_{42}O_2$ , leaflets, m. p.  $156^{\circ}$ , which is also formed when the lactone obtained by oxidation of the acid  $C_{24}H_{40}O_3$  is reduced by Clemmensen's method. The *methyl ester* of this acid,  $C_{25}H_{44}O_2$ , melts at  $56^{\circ}$ , and forms leaflets with a nacreous lustre.

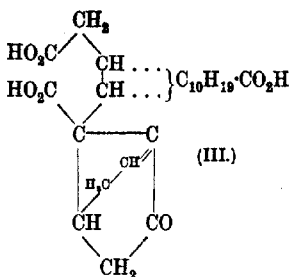
W. O. K.

**Bile Acids. XVI. Biliobanic Acid.** HEINRICH WIELAND and LEW FUKELMAN (*Z. physiol. Chem.*, 1923, **130**, 144-151).—



Biliobanic acid,  $C_{24}H_{34}O_7$ , obtained from cholic acid on oxidation

with bromine in alkaline solution, appears to have the formula (I).

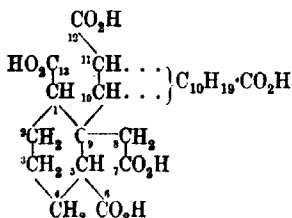


fuming nitric acid. *isoCilicianic acid*, when treated with concentrated sulphuric acid, yields an *unsaturated acid*,  $\text{C}_{23}\text{H}_{32}\text{O}_7$ , m. p. 320–321°, to which the annexed formula (III) is assigned. W. O. K.

**Bile Acids. XVII. *isoDeoxycholic Acid*.** HEINRICH WIELAND, ERNST HONOLD, and JOSÉ PASCUAL-VILA (*Z. physiol. Chem.*, 1923, 130, 326–337).—Ethyl cholate dissolved in ether and treated with carbonyl chloride yields a *chloro-carbonyl ester*,

$\text{COC}(\text{Cl})\cdot\text{O}\cdot\text{C}_{23}\text{H}_{38}\text{O}_2\cdot\text{CO}_2\text{Et}$ ,  
m. p. 140–141° (decomp.). When fused, this compound loses carbon dioxide and 3-*chloro-7:13-dihydroxycholanolic acid*,

$\text{C}_{24}\text{H}_{38}\text{O}_4\text{Cl}$ ,  
colourless needles, m. p. 196–197°, is formed; this may be converted by sodium in amyl-alcoholic solution into the unsaturated 7:13-*dihydroxycholanolic acid*,  $\text{C}_{24}\text{H}_{38}\text{O}_4$ , compact, glistening prisms, m. p. 216–217°. This compound is dimorphous, also forming slender needles, m. p. 181°, and it is reduced in acetic acid solution by hydrogen in presence of palladium to form  $\beta$ -*isodeoxycholic acid* (7:13-*dihydroxycholanolic acid*), slender needles, m. p. 226–227°. Oxidation of this acid with chromic acid results in the formation of *diketocholanolic acid*, m. p. 171–172° (ethyl ester, m. p. 149–151°). When this acid is oxidised by fuming nitric acid,  $\beta$ -*isocholoidanic acid* (annexed formula),  $\text{C}_{24}\text{H}_{36}\text{O}_{10}$ , is obtained, fine needles, m. p. 273°



(decomp.), whilst on oxidation with potassium permanganate, the first product is  $\psi$ -*deoxybilianic acid*,  $\text{C}_{24}\text{H}_{38}\text{O}_7$ , which on further oxidation yields  $\beta$ -*isocholoidanic acid*. *Methyl chlorocarbonyl deoxycholate*, from methyl deoxycholate and carbonyl chloride, forms needles, m. p. 137–138° (decomp.), whilst the corresponding derivative of ethyl deoxycholate melts at 114° (decomp.). *Methyl 3-chloro-7-hydroxycholate*, colourless needles, m. p. 121–122°.

results from heating methyl chlorocarbonyldeoxycholate. The chlorocarbonyl ester of cholesterol melts at 117–118°, and decomposes to form cholesteryl chloride, m. p. 86–90°. The chlorocarbonyl esters dissolved in ether, benzene, or ethyl acetate on treatment with ammonia yield the corresponding urethanes—that of methyl cholate, fine felted needles, m. p. 142° (*methyl phenetidine-urethane cholate*, needles, m. p. 172–173°); of methyl deoxycholate, m. p. 150–151°, and that of cholesterol, long needles, m. p. 217°.

W. O. K.

**The Synthesis of Hæmotricarboxylic Acid and a Hæmotetracarboxylic Acid.** WILLIAM KÜSTER [with A. HUGEL] (*Z. physiol. Chem.*, 1923, **130**, 1–23).—Ethyl cyanomethylsuccinate, b. p. 167–168°/25 mm., prepared by the condensation of ethyl bromoacetate with ethyl cyanoacetate in alcoholic solution in presence of sodium ethoxide, reacts with ethyl  $\beta$ -iodopropionate or ethyl  $\beta$ -chloropropionate in presence of sodium ethoxide to yield *ethyl  $\gamma$ -cyanopentane- $\alpha\gamma\delta$ -tricarboxylate*, a colourless, viscid oil, b. p. 208°/28 mm. When heated at 130–135° with alcohol containing sulphuric acid, *ethyl pentane- $\alpha\gamma\delta$ -tetracarboxylate* is obtained, a colourless, viscid liquid, b. p. 222°/12 mm., and from this ester on hydrolysis there are obtained two *pentane- $\alpha\gamma\delta$ -tricarboxylic acids* (*hæmotricarboxylic acids*). One has m. p. 177°, the other m. p. 140–141°; they are presumably the *cis*- and *trans*-forms, and are also obtained directly from the cyano-derivative by boiling it with dilute sulphuric acid. Attempts to resolve these acids through their brucine salts were unsuccessful. The following *brucine* salts of the acid, m. p. 177°, were obtained:  $(C_{22}H_{26}O_4N_2)_2 \cdot C_8H_{12}O_6 \cdot 4H_2O$ , long, prismatic needles, m. p. 154–156°,  $[\alpha]_D^{20} -29.5^\circ$  ( $c=2.5\%$  in water);

$(C_{22}H_{26}O_4N_2)_3 \cdot C_8H_{12}O_6 \cdot 4H_2O$ , thin, prismatic needles, m. p. 148–151°,  $[\alpha]_D^{20} -30.97^\circ$  ( $c=10\%$  in water), and of the acid, m. p. 140–141°, the *brucine* salt  $(C_{22}H_{26}O_4N_2)_2 \cdot C_8H_{12}O_6$ ,  $[\alpha]_D^{20} -20.31^\circ$  to  $-26.04^\circ$  ( $c=2.5$ – $3\%$  in water). The product of the bromination with phosphorus and bromine of the acid, m. p. 177°, is a mixture. If this mixture is hydrolysed with sodium hydroxide in presence of copper, an unsaturated tricarboxylic acid,  $\Delta^5$ -*pentene- $\alpha\gamma\delta$ -tricarboxylic acid*, may be isolated. This substance forms fine, prismatic needles, m. p. 112°, soluble in water, alcohol, ether, or acetic acid (*silver* salt,  $C_8H_7O_6Ag_3$ ). A *diethyl* ester,  $C_{12}H_{18}O_6$ , b. p. 206°/20 mm., is formed on boiling with absolute alcohol containing sulphuric acid, and on reduction of the acid with 2% sodium amalgam, the hæmotricarboxylic acid, m. p. 176–177°, was again obtained. In addition to this acid, a syrup was obtained, yielding an *acid*, isolated as the *calcium* salt,  $(C_8H_7O_7)_2Ca_3$ , and *silver* salt,  $(C_8H_7O_7Ag_3)$ , and on reduction a *new salt*,  $C_8H_9O_7Ag_3$ , was also obtained.

Similarly, when the acid, m. p. 140–141°, is brominated an isomeric *unsaturated acid*,  $C_8H_{10}O_6$ , rosettes of needles, m. p. 114° (*silver* salt,  $C_8H_9O_6Ag_3$ ), may be obtained from the product. This forms a *diethyl* ester,  $C_{12}H_{18}O_6$ , b. p. 199–201°/15 mm. From another fraction of the bromination product, when it is boiled with

40% potassium hydroxide solution, an acid is obtained, forming the *calcium* salt,  $(C_8H_7O_7)_2Ca_3$ , and the *silver* salt,  $C_8H_7O_7Ag_3$ , and on reduction a *calcium* salt,  $(C_8H_9O_7)_2Ca_3$ .

Condensation of ethyl cyanotricarballylate with ethyl iodo-propionate results in the formation of ethyl  $\gamma$ -cyanopentane- $\alpha\beta\gamma$ -tetracarboxylate, colourless oil, b. p. 227–228°/8–10 mm., and this when hydrolysed with concentrated hydrochloric acid yields pentane- $\alpha\beta\gamma$ -tetracarboxylic acid (*haemotetracarboxylic acid*), small, prismatic needles, m. p. 148° (*silver* salt,  $C_8H_9O_8Ag_4$ ; *copper* salt,  $C_8H_9O_8Cu_4$ , emerald-green precipitate; *barium* salt,  $[C_8H_9O_8]_2Ba_4$ ). The *anhydride*,  $C_8H_{10}O_7$ , was obtained on treatment of the acid with acetyl chloride. It forms a white powder, m. p. 220–221°. No pure product other than this haemotetracarboxylic acid was obtained from the hydrolysis mixture.

W. O. K.

**Production of Benzaldehyde and Benzoic Acid.** CARBIDE AND CARBON CHEMICALS CORPORATION (Brit. Pat. 197319).—A high yield of benzaldehyde or benzoic acid, or a mixture of the two, is obtained by the interaction of molecular oxygen (*e.g.*, air, oxygen) and dibenzyl, at a temperature of from 150° to 204°, in the absence of a catalyst.

W. T. K. B.

**Substitution in Vicinal Trisubstituted Benzene Derivatives.** II. WILLIAM DAVIES and LEON RUBENSTEIN (T., 1923, 123, 2839–2852).

**The Solubility of the Hydroxybenzaldehydes and the Hydroxytolualdehydes** NEVIL VINCENT SIDGWICK and ERIC NEWMARCH ALLOTT (T., 1923, 123, 2819–2826).

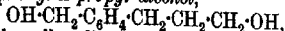
**Benzopolymethylene Compounds. X. Oxidation of  $\Delta^1$ -Dihydronaphthalene by Ozone.** JULIUS VON BRAUN and FRIEDRICH ZOBEL (*Ber.*, 1923, 56, [B], 2139–2142).— $\Delta^1$ -Dihydronaphthalene (*cf.* von Braun and Kirschbaum, A., 1920, i, 407) is readily oxidised to  $\beta$ -o-aldehydophenylpropaldehyde,



which is converted by dilute sulphuric acid into indene-2-aldehyde,  $C_9H_7 \cdot \begin{smallmatrix} CH \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} \cdot CHO$ . This is the first member of the indene series to be isolated which has a reactive group situated on the five-membered ring.

$\Delta^1$ -Dihydronaphthalene dissolved in glacial acetic acid is treated with ozone and the di-ozone decomposed by means of zinc dust. The product on distillation yields a resinous residue and  $\beta$ -o-aldehydophenylpropaldehyde, a colourless liquid, b. p. 153°/13 mm.,  $d_4^{20}$  1.142,  $n_D^{20}$  1.563, which becomes somewhat discoloured, but not otherwise appreciably altered when preserved. It does not readily yield crystalline derivatives with the customary reagents for aldehydes, but with aniline it gives the *dianil*,  $C_{22}H_{20}N_2$ , pale yellow crystals, m. p. 154°. It is oxidised by permanganate in alkaline suspension to o-carboxyphenylpropionic acid, m. p. 166°. It is

reduced by aluminium amalgam in the presence of moist ether to  $\gamma$ -o-hydroxymethylphenyl-n-propyl alcohol,



a very viscous, pale yellow liquid, b. p. about  $185^\circ/13$  mm., which, during distillation, suffers partial, intramolecular loss of water with production of  $\Delta^1$ -dihydronaphthalene. The aldehyde is converted by warm, dilute sulphuric acid (10%) into resinous products, (?) indene and indene-2-aldehyde. The yield of the latter is nearly 50% of that theoretically possible. It crystallises in colourless needles, m. p.  $50-51^\circ$ , which decompose rapidly when preserved. It is relatively stable towards acids, but very sensitive towards alkalis. The following derivatives are described: the *anil*, yellow leaflets, m. p.  $99^\circ$ ; the *p*-tolil, m. p.  $122^\circ$ ; the *oxime*, colourless needles, m. p.  $125-127^\circ$ ; the *semicarbazone*, m. p.  $237^\circ$ . It does not yield a well-crystallised derivative with phenylhydrazine or diphenylmethanedimethyldihydrazine.

H. W.

**3:4-Dimethylcyclopentan-1-one.** FRANZ FALTIS and HERMANN WAGNER (*Annalen*, 1923, **433**, 103-112).—3:4-Dimethylcyclopentan-1-one may be encountered as a product of the oxidation of hydrobixin; the ketone, which has never been described, has therefore been synthesised.

The action of a 15% solution of sodium iodide in acetone, at  $100^\circ$ , on  $\beta$ -bromobutyric acid, gives  $\beta$ -iodobutyric acid, which has m. p.  $32^\circ$  (corr.) (cf. Marx, *Diss.*, Freiburg i. B., 1881). A mixture of  $\beta$ -iodobutyric acid and two-thirds its weight of crotonic acid is heated at  $110^\circ$ , finally at  $135-140^\circ$ , with copper powder and ground pumice; the products of this reaction are two forms of  $\beta\beta'$ -dimethyladipic acid, (a) monoclinic leaflets, m. p.  $133^\circ$  (corr.), (b) snow-white, microcrystalline crusts, m. p.  $104-105^\circ$  (corr.), sinters  $102^\circ$ . From each acid a ketone is obtained by heating with acetic anhydride. The acid, m. p.  $133^\circ$ , gives a ketone, of which the *semicarbazone* forms colourless, slender, glistening needles, m. p.  $175-176^\circ$  (corr.), sinters and partly decomp.  $171^\circ$ ; the *semicarbazone* of the ketone from the acid, m. p.  $104-105^\circ$ , forms long, flat, lustrous needles, m. p.  $201-202^\circ$  (corr.) (decomp.), sinters  $195^\circ$ .

W. S. N.

**Condensation Products of Hemipinic Anhydride with Phenol Ethers and their Conversion into Anthracene Derivatives.** A. BISTRZYCKI and K. KRAUER (*Helv. Chim. Acta*, 1923, **6**, 750-770).—It was shown by Bistrzycki and Zen-Ruffinen (A., 1920, i, 436) that a number of phenylphthalide derivatives, including 3-*p*-hydroxyphenylmeconine, 3-*p*-methoxyphenylmeconine, and similar substances, cannot be reduced to the corresponding diphenylmethane derivative. It was suspected that reduction was hindered or prevented by the para-methoxy-group present in all these compounds, and this idea has now been confirmed by the preparation of a number of  $\psi$ -meconine derivatives having the para-position free. These compounds, which were obtained by condensing hemipinic anhydride with *o*- and *m*-tolyl methyl

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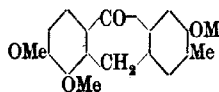
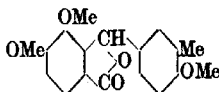
ethers and with veratrol and reducing the ketonic acids to the phthalides, can be readily reduced to the diphenylmethane derivatives.

4':5:6-Trimethoxy-3'-methylbenzophenone-2-carboxylic acid, obtained by condensing hemipinic anhydride with *o*-tolyl methyl ether by means of aluminium chloride, forms colourless, six-sided prisms, m. p. 218—219.5°. Its constitution follows from the work of Bistrzycki and de Schepper on the condensation of hemipinic anhydride with anisole (A., 1899, i, 151). Reduction of the compound with zinc and hydrochloric acid

in acetic acid solution gives 6'-methoxy-*m*-tolyl- $\psi$ -meconine (annexed formula), forming star-shaped aggregates of prisms, m. p. 128.5—129.5°. Reduction of this compound, or of the ketone, with finer zinc produces 4':5:6-trimethoxy-3'-methyl-*m*-tolyl- $\psi$ -meconine (annexed formula), which crystallises in fine needles, m. p. 129—130°. When this is dissolved in cold concentrated sulphuric acid it is rapidly converted into 3:7:8-trimethoxy-2-methyl-10-anthrone (annexed formula), which crystallises in bunches of colourless needles, m. p. 204—205°. This compound has no tendency to pass into the anthranol form, but by acetylation it gives 10-acetoxy-3:7:8-trimethoxy-2-methylanthracene, forming microscopic, yellow needles, m. p. 140°. Oxidation of the anthrone with chromic acid gives 3:7:8-trimethoxy-2-methylanthraquinone, yellow needles, m. p. 218°, which, when demethylated with aluminium chloride, gives 3:7:8-trihydroxy-2-methylanthraquinone, reddish-brown needles, m. p. 318—320°. When distilled with zinc dust, this gives 2-methylanthraquinone, which confirms the constitution of the anthrone given above; the alternative form of ring closure would give a 1-methylanthraquinone derivative. The constitution of the trihydroxymethylanthraquinone is also confirmed by its absorption spectrum, which, being very similar to that of flavopurpurin, confirms the methylflavopurpurin formula. 3:7:8-Triacetoxy-2-methylanthraquinone forms yellow needles, m. p. 204—205°.

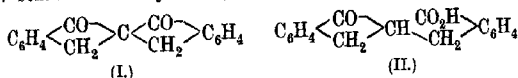
4':5:6-Trimethoxy-2'-methylbenzophenone-2-carboxylic acid, from hemipinic anhydride and *m*-tolyl methyl ether, has m. p. 167—169°, and forms a white, amorphous silver salt, sensitive to light. 6'-Methoxy-*o*-tolyl- $\psi$ -meconine crystallises in fine, white needles, m. p. 124—125°, and 4':5:6-trimethoxy-2'-methyl-*m*-tolyl- $\psi$ -meconine crystallises in fine, white needles, m. p. 136—138°, softening from 130°. From this was obtained 3:7:8-trimethoxy-1-methyl-10-anthrone, colourless needles, m. p. 163—164°, which on acetylation gives 10-acetoxy-3:7:8-trimethoxy-1-methylanthracene, yellow needles, m. p. 120°. Oxidation of the anthrone gives 3:7:8-trimethoxy-1-methylanthraquinone, yellow needles, m. p. 197°, giving by demethylation 3:7:8-trihydroxy-1-methylanthraquinone, very small, brown needles, m. p. above 330°.

Hemipinic acid was condensed with veratrole by Bentley and



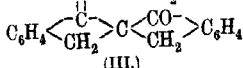
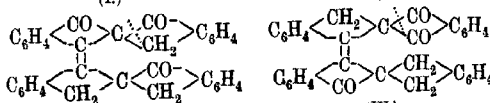
Weizmann (T., 1908, 93, 435), whose results are confirmed. Reduction of the condensation product gives 5':6'-dimethoxyphenyl- $\psi$ -meconine (annexed formula), colourless, microscopic needles, m. p. 132.5—133.5°, and 3':4':5:6-tetramethoxydiphenylmethane-2-carboxylic acid, colourless, microscopic needles, m. p. 145—147°. 1:2:6:7-Tetramethoxy-10-anthrone forms yellow, prismatic needles, m. p. 174—175°, and 10-acetoxy-1:2:6:7-tetramethoxyanthracene forms yellow, stellate aggregates of leaflets, m. p. 183—184°. The tetramethoxyanthraquinone obtained by Bentley and Weizmann (*loc. cit.*) when demethylated gives 1:2:6:7-tetrahydroxyanthraquinone, brownish-orange needles, m. p. above 330°. E. H. R.

**Spirans. VIII. Dibenzylindandione and the Constitution of Coloured Anhydroindandiones.** DAN RADULESCU and I. TANASESCU (*Bul. Soc. Stiinte Cluj*, 1922, 1, 185—191; from *Chem. Zentr.*, 1923, iii, 137—138; cf. A., 1913, i, 37).—It has been shown (*loc. cit.*) that the spiran I is hydrolysed by an alkali to the acid II, from which the spiran, I, can again be obtained by elimination of water. The coloured anhydro-derivatives III and IV behave differently. They give an intense blue coloration with

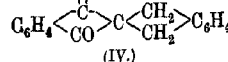


(I.)

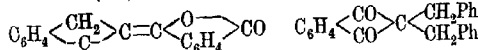
(II.)



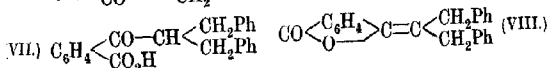
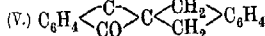
(III.)



(IV.)



(VI.)



alkali hydroxides. The structural analogy of the two compounds is shown by the similarity of their absorption spectra. Both compounds give acids of the same formula,  $\text{C}_{24}\text{H}_{24}\text{O}_4$ , probably by fission at the dotted line. The acid obtained from the compound IV does not apparently yield the spiran again on dehydration, but a compound of different properties having the composition indicated by formula V. The authors synthesised the compound VI, which by hydrolysis yields the compound VII. The latter is very similar to II, but on dehydration yields VIII. The formation of a lactone ring is to be expected in this case on stereochemical grounds. In the case of the acid II, lactone formation results in a ring with seven carbon atoms which by rearrangement gives the

more stable system I. The compound VI, like the dialkylindandiones, does not give ketone reactions and yields with strong sulphuric acid anhydro-compounds analogous to III and IV.

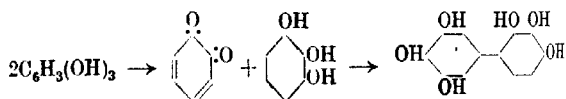
2:2-Dibenzylindandione (VI) is obtained from the reaction of sodium ethoxide (2 mols.) with diketohydrindene (1 mol.) and benzyl chloride (2 mols.). It forms needles, m. p. 158—158.5°. By treatment with potassium hydroxide and subsequent acidification,  $\beta$ -diphenylpropanephthaloylic acid (VII) is obtained as an amorphous, transparent mass. Dehydration of the last compound gives the *keto-lactone* (VIII) which forms snow-white, silky crystals, with m. p. 131°.

G. W. R.

**Products of the Destructive Distillation of Sodium Anthraquinone-1- and -2-sulphonates.** ARTHUR GEORGE PERKIN and WILLIAM GAWAN SEWELL (T., 1923, 123, 3032—3040).

**The Constitution of Purpurogallin.** RICHARD WILLSTÄTTER and HUGO HEISS (*Annalen*, 1923, 433, 17—33).—Perkin's formula for purpurogallin (P., 1913, 29, 354) does not account for the indifference of the carbonyl group in its ethers, and does not help to elucidate the mechanism of its formation by the oxidation of pyrogallol. An alternative formula, free from these defects, is now suggested.

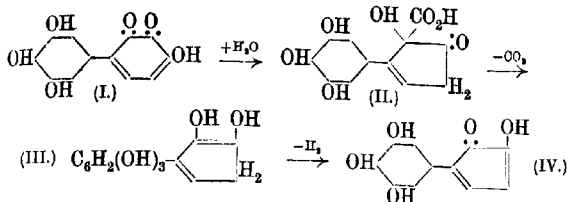
The first step in the formation of purpurogallin is the production of 3-hydroxy-*o*-benzoquinone. A dimeric form of this substance has been isolated by Perkin and Steven (T., 1906, 89, 802; cf. Perkin, *loc. cit.*, also T., 1913, 103, 650, and Willstätter and Müller, A., 1911, i, 728) by the oxidation of pyrogallol by means of quinone, or of amyl nitrite and acetic acid; it is converted into purpurogallin with difficulty, by boiling with water. In the presence of an excess of pyrogallol, however, the hydroxyquinone can become stabilised in a different manner, isomerisation to 3:4:5-triketo- $\Delta^1$ -cyclohexene being followed by condensation of the latter with a further molecule of pyrogallol. The product of this reaction,



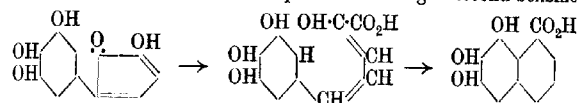
a hexahydroxydiphenyl for which the above formula is preferred, is then oxidised to give an *o*-quinone (I), which undergoes a kind of benzilic acid rearrangement, similar to the formation of croconone acid from rhodizonic acid, with formation of the *cyclopentenone* derivative (II). Carbon dioxide is eliminated spontaneously from (II), and the resulting dihydroxypentadiene derivative (III) is then oxidised to purpurogallin (IV).

This explanation of the mechanism of the formation of purpurogallin receives support from the following facts. Purpurogallin monomethyl ether is formed by oxidising a mixture of pyrogallol and its 1-methyl ether, or of pyrogallol and 3-methoxy-*o*-quinone; the latter may be taken as such, or produced *in situ* by oxidising pyrogallol methyl ether. But 3-methoxy-*o*-quinone, which cannot

isomerise to a triketocyclohexane derivative, and therefore cannot undergo condensation to a diphenyl derivative, cannot be further



oxidised, alone, to purpurogallin dimethyl ether. Moreover, in the oxidation of gallic acid, from two molecules one molecule of carbon dioxide is eliminated. This is readily comprehensible, because if the dicarboxylic acid (annexed formula), formed by the condensation of gallic acid with its *o*-quinone, passes next into the enol form, one carboxyl group will be spontaneously eliminated. Further transformation of the resulting monocarboxylic acid will give purpurogallincarboxylic acid. Purpurogallin is converted into the isomeride, purpurogallone (Perkin, *loc. cit.*) by heating with alkali. This is explained as being a second benzilic



acid transformation; the conversion of purpurogallincarboxylic acid into purpurogallonecarboxylic acid doubtless follows a similar course.

Incidentally, the methyl ester of purpurogallincarboxylic acid is prepared by direct esterification of the acid, or by the oxidation of methyl gallate in aqueous-alcoholic solution by means of peroxydase and hydrogen peroxide. It forms dark brownish-red, rhombic (or monoclinic or triclinic) prisms, decomp.  $260-270^\circ$ , after darkening at  $240^\circ$ . In the presence of alkali and air, it gives an intense blue coloration, which changes to cyanine-red on addition of mineral acid.

W. S. N.

**Production of Dinitroperylenequinone.** HANS PEREIRA (Brit. Pat. 199720).—Perylenequinone or mononitroperylenequinone is nitrated, e.g., with a boiling mixture of glacial acetic acid and nitric acid (*d* 1.4). [*Cf. J.S.C.I.*, 1923, Dec.] W. T. K. B.

**Steric Hindrance; Study of the Double Bond of some Ethylenic Camphor Derivatives by Means of Catalytic Hydrogenation.** JEAN DÉTRIE (*Bull. Soc. chim.*, 1923, [iv], 33, 1263-1284).—Hydrogenation of *d*-ethylidenecamphor, *d*-hexahydrobenzylidenecamphor, *d*-benzylidenecamphor, *d*-methylsilylidenecamphor,

camphor, *d*- and *l*-anisylidenecamphor in presence of finely divided platinum leads to the conclusion that the reduction of the ethylenic bond takes place more readily when it is situated between a ring and a side-chain than when between two rings. In the latter case, the velocity of hydrogenation depends on the position of substituents in the ring, being less when the substituent is in the ortho-position with respect to the carbon atom linked to the double bond than when the substituent occupies the para-position. The following are described: *o*-methoxyhexahydrobenzylcamphor,  $C_{18}H_{30}O_2$ , a syrupy liquid, b. p. 185–190°/12 mm.,  $d^{20}_D$  0.99,  $[\alpha]_D^{20} +54^\circ$ ; hexahydroanisylcamphor,  $C_{18}H_{30}O_2$ , b. p. 185–190°/12 mm.,  $d^{20}_D$  0.98.

H. J. E.

**Demonstration of Tautomeric Forms by Means of Catalytic Reduction.** GUIDO CUSMANO and ROSALBA BOCCUCCI (*Gazzetta*, 1923, 53, 649–657).—Reduction of buchu-camphor by means of hydrogen in presence of platinum black at the ordinary temperature yields two geometric isomerides of 3-hydroxytetrahydrocarvone,  $CHMe < \begin{smallmatrix} CO-CH(OH) \\ CH_3-CH_2 \end{smallmatrix} > CHPr^s$ , together with other products, including probably the glycol obtained by Kondakov and Bachtshéev (A., 1901, i, 334) by reducing buchu-camphor by means of sodium amalgam. It is therefore evident that buchu-camphor does not react exclusively in accordance with the formula proposed by Semmler and McKenzie (A., 1906, i, 373). Each of the two 3-hydroxytetrahydrocarvones yields the same two isomeric 3-bromotetrahydrocarvones, both of these giving tetrahydrocarvone on reduction.

*Isomeride* (1) of 3-hydroxytetrahydrocarvone is a mobile liquid, b. p. 234°, with a burning taste and the odour of mint; its *semicarbazone* forms colourless, rectangular plates, sometimes twinned, m. p. 180–181° (decomp.), and its *oxime*, long, colourless needles, m. p. 120–121°. *Isomeride* (2), obtained in only small amount, gives a *semicarbazone* which forms rosettes of prismatic crystals, m. p. 225° (decomp.), tends to undergo pulverisation, and rapidly becomes yellow in the light.

The liquid 3-bromotetrahydrocarvone,  $CHMe < \begin{smallmatrix} CO-CHBr \\ CH_2-CH_2 \end{smallmatrix} > CHPr^s$ , has b. p. 136–140°/5 mm.; the solid isomeride forms a lustrous, white powder, m. p. about 125°, and undergoes gradual alteration.

T. H. P.

**Piperitone. VI. The Reduction of Piperitone.** REGINALD SLATER HUGHESDON, HENRY GEORGE SMITH, and JOHN READ (T., 1923, 123, 2916–2925).

**Pinane.** A. LIPP (*Ber.*, 1923, 56, [B], 2098–2107).—The hydrogenation of pinene in the presence of nickel according to Sabatier and Senderens and of platinum according to Foken and Willstätter has been examined. Although the steric uniformity of the pinane thus produced is not established, the results point to the conclusion that the former method yields mainly *trans*-

derivatives with lower density and index of refraction, whereas the latter process gives *cis*-compounds with higher density and index of refraction (cf. Auwers, A., 1919, i, 578; Skita, A., 1920, i, 832). It is placed beyond doubt that the carbon skeleton of pinene remains intact in pinane.

A sample of pinene having  $[\alpha]_D -38.08^\circ$  obtained from French oil of turpentine is converted by hydrogen in the presence of nickel at  $220-230^\circ$  into pinane,  $C_{10}H_{18}$ , which, after being treated with alkaline potassium permanganate solution, has b. p.  $162-164/720$  mm.,  $d_4^{20}$  0.8519,  $n_D^{20}$  1.45942,  $[\alpha]_D -16.1^\circ$ ; it is stable towards air or permanganate solution. In the presence of platinum black, *d*-pinene,  $[\alpha]_D +47.5^\circ$ , gives a pinane, b. p.  $163-164/720$  mm.,  $d_4^{20}$  0.8566,  $n_D^{20}$  1.4624,  $[\alpha]_D +23.080$ , whereas *l*-pinene gives a product, b. p.  $164.8-165.8/716$  mm.,  $d_4^{20}$  0.8562,  $n_D^{20}$  1.4620,  $[\alpha]_D -18.9^\circ$ . This product undergoes alteration in boiling point and particularly in density, although its composition remains unchanged when it is passed over nickel pumice at  $200-205^\circ$ .

The action of bromine on pinane dissolved in glacial acetic acid leads to the production of a tetrabromide,  $C_{10}H_{16}Br_4$ , a viscous, reddish-brown liquid which is possibly not homogeneous; it appears to be a monocyclic substance and therefore only indirectly related to pinane. In spite of the presence of the tetramethylene ring, pinane is very stable toward solutions of hydrogen chloride or bromide in glacial acetic acid, by which it is converted above  $230^\circ$  into non-homogeneous products. Hydriodic acid reduces it with difficulty to hydroaromatic substances containing small proportions of aromatic hydrocarbons. The behaviour of pinane thus resembles closely that of pinene.

The oxidation of pinane dissolved in glacial acetic acid by solid potassium permanganate at  $28-30^\circ$  leads to the production of

$$\begin{array}{l} \text{CH}_2-\text{CH} \\ | \quad | \\ \text{CH}_2 \quad \text{CMe}_2 \\ | \quad | \\ \text{OH}-\text{CMe}-\text{CH} \end{array} \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array}$$
*methylpinol* (annexed formula), colourless, very volatile needles, m. p.  $79^\circ$ , b. p.  $93-95/13$  mm.,  $204-205/721$  mm.,  $[\alpha]_D -24.39^\circ$  in ethereal solution, which is regarded as a stereoisomeride of Wallach's methylpinol, m. p.  $58-59^\circ$  (cf. A., 1907, i, 936), since, like this substance, it is readily converted into terpen hydrate by cold dilute sulphuric acid. The acidic products of the oxidation of pinane include pinonic acid and small quantities of terebic acid. When treated with concentrated nitric acid (*d* 1.4) at the temperature of boiling water, pinane is converted into terebic, (?) norpinic, terephthalic, and oxalic acids. Pinonic acid is isolated from the products of the oxidation of pinane by chromium trioxide in glacial acetic acid solution.

H. W.

#### The Nature of the Products of Fractionation of some Turpentine and the Constants of their Pure Constituents.

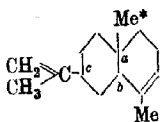
G. DUPONT and L. DESALBRES (*Bull. Soc. chim.*, 1923, [iv], 33, 1252-1262).—A series of fractionations of pinenes obtained from both Bordeaux and Aleppo turpentine with an examination of the optical properties of the fractions obtained led to the conclusion

that a partial separation of the optically active isomerides had been effected. Similar results were obtained by a series of fractional crystallisations. Synthetic mixtures of active and inactive pinene yielded corroborative evidence. An investigation of inactive pinene showed it to be a single substance and not racemic. Physical constants of the turpentines from both sources are given from which calculations of those for the pure pinenes are made, the data used being based on the yields of nitrosocchloride obtainable from the mixture.

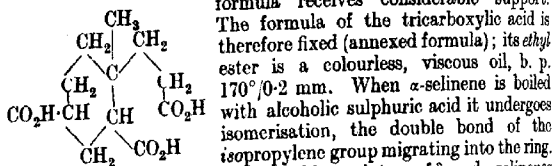
H. J. E.

**Higher Terpene Compounds. XIV. Selinene and the Sesquiterpene Alcohols of Celery-seed Oil.** L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1923, 6, 846—855).—In a previous

paper (this vol., i, 119), the constitution given in the annexed formula was provisionally assigned to  $\alpha$ -selinene. The methyl group\* attached to the quaternary carbon atom (a) might conceivably be attached to one of the other quaternary carbon atoms (b) or (c). It is now shown that the tricarboxylic acid obtained

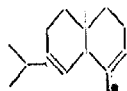


by oxidation of  $\alpha$ -selinene can be readily esterified and the triethyl ester can be readily hydrolysed. The ready esterification of the acid precludes the possibility that either carboxyl group is attached to a tertiary carbon atom, and since the only formula for  $\alpha$ -selinene which will give such a tricarboxylic acid is that given above, the formula receives considerable support.

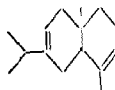


The formula of the tricarboxylic acid is therefore fixed (annexed formula); its ethyl ester is a colourless, viscous oil, b. p. 170°/0.2 mm. When  $\alpha$ -selinene is boiled with alcoholic sulphuric acid it undergoes isomerisation, the double bond of the isopropylene group migrating into the ring.

The product of the reaction is probably a mixture of  $\delta$ - and  $\epsilon$ -selinenes of the formula

 $\delta$ -Selinene.

and

 $\epsilon$ -Selinene.

The product forms a colourless oil, b. p. 130°/12 mm.,  $d_4^{20}$  0.9234;  $n_D^{20}$  1.5167. By dehydrogenation with sulphur, it gives a much higher yield of eudalene than  $\alpha$ -selinene. It is improbable that the two double bonds form a conjugated system in one ring. Attempts to hydrogenate the inverted selinene with sodium and amyl alcohol were unsuccessful, whereas this treatment will reduce a cyclic conjugated system.

From the fraction of celery-seed oil, b. p. 140—170°/12 mm., was isolated a small quantity, about 1% of the original oil, of a sesquiterpene alcohol, b. p. 157—164°/12 mm., having the com-

position  $C_{15}H_{24}O$ ,  $[\alpha]_D +4.7^\circ$ ,  $d_4^{20}$  0.9618,  $n_D^{20}$  1.5049. Evidence was obtained of the presence of a primary or secondary and of a tertiary alcohol. No naphthalenic hydrocarbon could be obtained by dehydrogenation with sulphur.

[With FR. LIEBL and S. PONTALTI.] *Attempts to dehydrogenate some sesquiterpenes.*—Hydrocarbons derived from hydrogenated naphthalene can be dehydrogenated with sulphur at  $180$ – $250^\circ$ , and the naphthalene hydrocarbon can be detected by means of its picric acid compound. This procedure has been applied to caryophyllene, santalene, and cedrene, none of which is found to be a naphthalene derivative.

E. H. R.

**Higher Terpene Compounds. XV. The Sesquiterpene Fractions of Hyssop Oil, *Eucalyptus globulus* Oil, and Gurjun Balsam; and Guaiacol.** L. RUZICKA, S. PONTALTI, and FR. BALAS (*Helv. Chim. Acta*, 1923, 6, 855–865).—The fraction of hyssop oil boiling between  $110^\circ$  and  $180^\circ/12$  mm. contains both a hydrocarbon and alcohols of the sesquiterpene series. The hydrocarbon,  $C_{15}H_{24}$ , when finally freed from oxygen-containing compounds by treatment with permanganate, formed a colourless oil, b. p.  $125^\circ/12$  mm.,  $d_4^{20}$  0.9116,  $n_D^{20}$  1.5012. By dehydrogenation with sulphur, it was converted into cadalene, which was identified by its picrate and styphnate. The sesquiterpene of hyssop oil, forming 2–3% of the oil, is therefore of the cadinene type. The sesquiterpene alcohol fraction obtained by redistillation of the  $110$ – $180^\circ/12$  mm. fraction contained a primary or secondary alcohol, b. p.  $150^\circ/12$  mm., and a tertiary alcohol (not reacting with phthalic anhydride), forming a green, viscous oil, b. p.  $150$ – $152^\circ/12$  mm.,  $d_4^{20}$  0.9784,  $n_D^{20}$  1.5096. Its formula is probably  $C_{15}H_{26}O$ . By loss of water, it forms a sesquiterpene which appears to be the same as that described above. The sesquiterpene compounds of *Eucalyptus globulus* oil also belong to the cadinene type, unlike other eucalyptus oils, which are of the eudesmol type.

The sesquiterpene alcohol, guaiacol, obtained from gum guaiacum and other sources, does not react with phthalic anhydride and is therefore probably a tertiary alcohol. It can be dehydrated by heating with 85% formic acid, forming a sesquiterpene, b. p.  $128$ – $130^\circ/12$  mm.,  $[\alpha]_D -16.8^\circ$ ,  $d_4^{20}$  0.9116,  $n_D^{20}$  1.5022. By dehydrogenation of this oil with sulphur, a blue oil, b. p.  $130$ – $160^\circ/12$  mm. was obtained, giving a picrate crystallising in black needles, m. p.  $115^\circ$ . This does not correspond with a naphthalene hydrocarbon.

The sesquiterpenes from gurjun balsam,  $\alpha$ - and  $\beta$ -gurjunene, are probably tricyclic compounds; but when the hydrochloride of gurjunene is treated with sodium acetate, the regenerated hydrocarbon has constants corresponding with a hydronaphthalene derivative, b. p.  $123$ – $129^\circ$ ,  $d_4^{20}$  0.9233,  $n_D^{20}$  1.5105,  $[\alpha]_D -39.0^\circ$ . By catalytic hydrogenation, it forms a hydrocarbon,  $C_{15}H_{22}$ , b. p.  $125$ – $130^\circ$ ,  $d_4^{20}$  0.9021,  $n_D^{20}$  1.4910. By dehydrogenation with sulphur, however, it did not give a naphthalene hydrocarbon. If it is, after all, a naphthalene derivative; its behaviour with sulphur is exceptional.

E. H. R.

**Properties of Loroglossin and its Products of Hydrolysis; Glucose and Loroglossigenin.** MARC BRIDEL and PIERRE DELAUNAY (*Compt. rend.*, 1923, 177, 776—778).—Air-dried loroglossin,  $C_{30}H_{48}O_{18}$ , contains 6.26% of water, which it loses at 50° in a vacuum. When heated, it shrinks at 133.5°, and becomes transparent at 143.4°. It has  $[\alpha]_D -45.65^\circ$ , its solution has saponin-like properties, and gives no precipitate with Goulard's extract. On hydrolysis by emulsin, loroglossin affords 2 mols. of dextrose and 1 mol. of loroglossigenin, m. p. 77°, soluble in cold 5% sodium hydroxide solution, and giving a feeble violet coloration with ferric chloride. Loroglossigenin is non-reducing; its solution in concentrated sulphuric acid has the same colour as that of a similar solution of loroglossin.

E. E. T.

**The Constitution of Cantharidin. II.** SAMUEL COFFEY (*Rec. trav. chim.*, 1923, 42, 1026—1032; cf. this vol., i, 695).—The author's previous difficulty with the sulphonation of *p*-xylic acid has been overcome by modifications in the experimental method. The chief impurity in the product is sulphur, which was removed by conversion into thiosulphate, and finally by sublimation over molecular silver. Small quantities of dimethylhexahydrophthalic acid were obtained, however, and shown not to be identical with deoxycantharidic acid, thus showing that Gadamer's formula for cantharidin is correct.

H. H.

**The Preparation of Melanins containing Nitrogen.** OSKAR ADLER (*Biochem. Z.*, 1923, 141, 304—309).—By treatment of *p*-aminobenzoic acid with hydrogen peroxide and ferric chloride (this vol., i, 591), a 56% yield of *p*-aminobenzoic-melanic acid was obtained in the form of a black powder, soluble in alkalis or alcohol, and insoluble in dilute acid, ether, or light petroleum. On heating the melanic acid at 270° for one hour, it was converted into *p*-aminobenzoic-melanin, a black, amorphous powder. From tyrosine, by similar methods, tyrosine-melanic acid and tyrosine-melanin were prepared. Both melanins were insoluble in dilute alkalis, acids, or organic solvents.

J. P.

**Tannins. III. Turkish Tannin.** P. KARRER, ROSA WIDMER, and MAX STAUB (*Annalen*, 1923, 433, 288—305).—It is shown that Turkish tannin is even less homogeneous than Chinese tannin (cf. Karrer, Salomon, and Peyer, this vol., i, 352; also Fischer and Freudenberg, A., 1915, i, 437). By fractional precipitation by means of aluminium hydroxide, it can be separated into fractions, for which  $[\alpha]_D$ , in alcohol, varies between +15.7° and +43.7°. The yield of dextrose, obtained by hydrolysing for seventy hours by means of 5% sulphuric acid does not vary much from fraction to fraction, but the higher the rotation of the fraction taken the more gallic acid and the less ellagic acid are obtained. Since the dextrose and ellagic acid contents are not parallel, it is evident that the acid is not present as a simple glucoside. Moreover, if it were present in that form, the tannin fraction containing more of it should, on being methylated by means of diazomethane, and

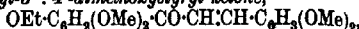
then acetylated by heating with sodium acetate and acetic anhydride, give a higher value when the acetyl was estimated; but this is not so. Thus it seems likely that the ellagic acid is present actually as part of the tannin molecule, perhaps partly replacing gallic acid.

In contrast with Chinese tannin, Turkish tannin is not fully galloylated. This is shown as follows. 1-Acetyltetra(triacetyl-galloyl)glucose can be obtained by the successive action of cold glacial acetic acid-hydrobromic acid, acetyl bromide, and acetic anhydride-sodium acetate at 100°, on samples of pentagalloylglucose obtained from penta(triacetyl-galloyl)glucose by (a) acid hydrolysis, (b) alkaline hydrolysis. Samples prepared in the latter way contain free gallic acid, which actually separates during the first operation. Hence the deduction is drawn that pure 1-acetyltetra(triacetyl-galloyl)glucose can be obtained by the method outlined, provided the starting material contains some completely galloylated dextrose. But when these reactions are applied to various fractions of Turkish tannin, pure 1-acetyltetra(triacetyl-galloyl)glucose,  $[\alpha]_D + 43^\circ$  to  $+45^\circ$ , is not obtained; instead, more soluble products are obtained, for which  $[\alpha]_D$  varies between  $+56.7^\circ$  and  $+77.88^\circ$ , whilst the acetyl content varies between 43% and 44%. Clearly, the sugar (not necessarily dextrose, although this is assumed) present in Turkish tannin is combined with a varying number of gallic acid molecules. Probably 25–30% of the gallic acid is depsidic, the remainder being in direct combination with the dextrose molecule. W. S. N.

**Tannins and Similar Substances. XIV. The Carbon Skeleton of Catechin.** KARL FREUDENBERG and ERNST COHN (*Ber.*, 1923, 56, [B], 2127–2131).—The identity of synthetic 2:4:6:3':4'-pentamethoxy- $\alpha$ -y-diphenylpropane with the ether obtained by Kostanecki and Lampe (*A.*, 1907, i, 73, 334; 1908, i, 86) from Gambier catechu has caused Freudenberg (*A.*, 1920, i, 752) to consider that the catechins are derived from  $\alpha$ -y-diphenylpropane, but this hypothesis has been doubted by Nierenstein (*T.*, 1920, 117, 972, 1156; 1921, 119, 164; 1922, 121, 601; this vol., i, 124). Additional evidence in favour of the conception is now adduced.

Tetramethyl-*d*-catechin is reduced by sodium and alcohol, and the crude phenol which is thereby produced is transformed by *p*-nitrobenzoyl chloride and sodium hydroxide into 6-*p*-nitrobenzoxy-2:4:3':4'-tetramethoxy- $\alpha$ -y-diphenylpropane, lemon-yellow prisms, m. p. 141–142°; this is hydrolysed by aqueous sodium hydroxide solution to 2-hydroxy-4:6:3':4'-tetramethoxy- $\alpha$ -y-diphenylpropane, coarse, colourless prisms, m. p. 89–90°, which is thus obtained in the crystalline condition. It is converted by ethyl sulphate and potassium hydroxide into 2:4:3':4'-tetramethoxy-*i*-ethoxy- $\alpha$ -y-diphenylpropane, m. p. 49–50°. The synthesis of the latter compound is effected in the following manner. 2:4-Dimethyl-chloracetophenone is transformed by ethyl sulphate and potassium hydroxide into 2:4-dimethyl-6-ethylphloracetophenone, colourless needles, m. p. 73–74°, which condenses with veratraldehyde in the

presence of alcohol and sodium hydroxide solution to 2 : 4-dimethoxy-6-ethoxyphenyl-3' : 4'-dimethoxystyryl ketone,



sulphur-yellow, rectangular platelets, m. p. 136—137°. The compound is reduced by hydrogen in the presence of spongy platinum to 2 : 4 : 3' : 4'-tetramethoxy-6-ethoxy- $\alpha$ -diphenylpropane, m. p. 49—50°, which is identical in all respects with the product derived from the catechin.

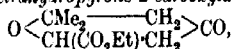
2-Hydroxy-4 : 6-dimethoxyphenyl  $\beta$ -3' : 4'-dimethoxyphenylethyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})_2$ , colourless platelets, m. p. 125—126°, is prepared by the catalytic reduction of 2-hydroxy-4 : 6-dimethoxyphenyl 3' : 4'-dimethoxystyryl ketone in the presence of platinum; it is converted by ethyl sulphate into 2 : 4-dimethoxy-6-ethoxyphenyl  $\beta$ -3' : 4'-dimethoxyphenylethyl ketone, long needles, m. p. 89—90°. The oxygen atom of the carbonyl groups of these compounds could not be replaced by hydrogen.

H. W.

**Tetrahydro- $\gamma$ -pyrones. III. Catalytic Hydrogenation of Mesityloxidoxalic Esters.** W. BORSCH and K. THIELE (*Ber.*, 1923, 56, [B], 2132—2135).—The catalytic hydrogenation of ethyl  $\alpha$ -mesityloxidoxalate occurs much more rapidly than that of the corresponding  $\beta$ -compound. This is in harmony with Dieckmann's conception (*A.*, 1920, i, 813), that the  $\alpha$ -variety is an open-chain compound, whereas the  $\beta$ -form is a derivative of  $\gamma$ -pyrone.

Ethyl  $\alpha$ -mesityloxidoxalate is converted by the hydrochloride of phenylcarbamhydrazide and sodium acetate into ethyl 1-carbamido-3-isobutylene-pyrazole-5-carboxylate, colourless needles, m. p. 238—239°, and by 2-nitro-4-cyanophenylhydrazine into ethyl 2'-nitro-4'-cyanophenyl-3-isobutylene-pyrazole-5-carboxylate, slender, pale yellow needles, m. p. 190°. It is converted by hydrogen in the presence of colloidal palladium into ethyl  $\alpha$ -hydroxy- $\gamma$ -keto- $\alpha$ -methyl- $\Delta^5$ -heptenoate,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$ , an almost colourless liquid, b. p. 130—133°/20 mm. (the copper derivative,  $[\text{C}_{10}\text{H}_{15}\text{O}_4]_2\text{Cu}$ , crystallises in green needles, m. p. 151—152°). The ester is also prepared by the action of sodium on an ethereal solution of methyl isobutyl ketone and ethyl oxalate, and is further characterised by its 2-nitro-4-cyanophenylhydrazone,  $\text{C}_{17}\text{H}_{20}\text{O}_5\text{N}_4$ , slender, pale yellow needles, m. p. 184—185°.

Ethyl  $\beta$ -mesityloxidoxalate is very slowly hydrogenated in alcoholic solution in the presence of colloidal palladium to ethyl 6 : 6-dimethyl-4-ketotetrahydropyrone-2-carboxylate,



a pale yellow liquid, b. p. 150—152°/18 mm., which does not show any tendency to crystallise and possibly contains small quantities of unreduced original material.

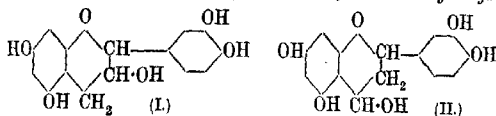
The phenylcarbamhydrazone of ethyl  $\beta$ -mesityloxidoxalate,  $\text{C}_{17}\text{H}_{21}\text{O}_5\text{N}_3$ , crystallises in colourless, lustrous needles, m. p. 219°, whereas the 2-nitro-4-cyanophenylhydrazone,  $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_4$ , forms red prisms, m. p. 175°.

H. W.

**The Constitution of Catechin.** I. JAMES J. DRUMM (*Proc. Roy. Irish Acad.*, 1923, 36, 41—49).—Phosphorus pentachloride acts vigorously on catechin tetramethyl ether to give the *chloride of catechin tetramethyl ether*, m. p. 112°, which, when heated rapidly, loses hydrogen chloride to give *dehydrocatechin tetramethyl ether*,  $C_6H_2(OMe)_2 \begin{smallmatrix} \diagup O-CH-C_6H_3(OMe)_2 \\ \diagdown CH:CH \end{smallmatrix}$ , m. p. 133.5—134.5°. When this

compound is treated with bromine in chloroform solution, hydrogen bromide is evolved and a bright red, crystalline *monobromide*, to which the formula  $C_6H_2(OMe)_2 \begin{smallmatrix} \diagup O-Br-C_6H_3(OMe)_2 \\ \diagdown CH-CH \end{smallmatrix}$  is assigned, is precipitated.

This monobromide, on treatment with alcoholic ammonia, yields a colourless base, m. p. 133—134°, which, on treatment with a chloroform solution of hydrogen chloride, yields its *anhydrohydro-*



*chloride*, m. p. 126—128°. It is considered that either formula I or II represents the structure of catechin. *Ethylcatechin tetramethyl ether*, m. p. 123°, and *n-butylcatechin tetramethyl ether*, m. p. 79—80°, were also prepared. H. H.

**Synthesis of Derivatives of Phenothioxin.** SRI KRISHNA (*T.*, 1923, 123, 2782—2786).

**Derivatives of Thionaphthacourmarin.** SAMUEL SMILES and LESLIE RALPH HART (*T.*, 1923, 123, 2907—2913).

**Synthesis of Substituted Thianthrens.** II. SRI KRISHNA (*T.*, 1923, 123, 2786—2790).

**The Distribution Equilibrium of Quinine between Water and Ether at 0°.** W. D. TREADWELL [with R. GONSETT and A. TRIPET] (*Helv. Chim. Acta*, 1923, 6, 744—749).—Measurements of the distribution of quinine between water and ether at 0° show that the usual distribution law is followed, the molecular weight of quinine in ethereal solution being twice the molecular weight in aqueous solution. The solubility of quinine is 1 part in 188 parts of absolute ethyl ether and 1 part in 15 parts of ether saturated with water. The very divergent solubilities given in the literature are probably due to the use of ether containing varying proportions of water. E. H. R.

**The Alkaloids of the Java Coca Leaf.** A. W. K. DE JONG (*Rec. trav. chim.*, 1923, 42, 980—999).—A method is described by which the alkaloids (mainly cocaine and tropacocaine) may be extracted from coca leaves by means of ammoniacal benzene at 55°. The alkaloids are decomposed by boiling with mineral acid, and the ecgonine produced may be estimated polarimetrically. The following rotatory powers are quoted: ecgonine monohydrate

$[\alpha]_D$  -45.6°, hydrochloride  $[\alpha]_D$  -47.1°, anhydrous benzoylcegonine  $[\alpha]_D$  -63.3°, anhydrocegonine  $[\alpha]_D$  -84.6°. Anhydrocegonine hydrochloride exhibits mutarotation. *Ecgonine benzoate* has m. p. 145°, *tropacocaine benzoate*, m. p. 60–61°. The hydrochlorides of ecgonine and of anhydrocegonine both form *pentamercurichlorides*, whilst  $\psi$ -tropine hydrochloride forms a *dimercurickloride*. H. H.

**Preparation of Creatinine from Creatine.** GRAHAM EDGAR and W. S. HINEGARDNER (*J. Biol. Chem.*, 1923, **56**, 881–886).—Creatine is converted into creatinine hydrochloride (a) by evaporating its solution in hydrochloric acid to dryness, (b) by treating the anhydrous substance with gaseous hydrogen chloride, or (c) by heating it in a closed vessel on a steam-bath for twenty-four hours with a slight excess of hydrochloric acid. Free creatinine is then obtained either by saturating a concentrated solution of the hydrochloride with ammonia or by adding the solid salt to its own weight of concentrated ammonia, cooling in ice, and filtering. Creatinine is best crystallised by dissolving in 5 parts of water previously heated at 65°, adding twice the volumes of acetone, and cooling to 0°. E. S.

**Constitution of Morphine.** HEINRICH WIELAND and ERNST KOBALKEK (*Annalen*, 1923, **433**, 267–271).—The experimental results are given of an uncompleted attempt to carry out the degradation of methyltetrahydromorphimethine by progressive methylation. The reduction of codeine in alcoholic solution by means of palladium black and hydrogen gives, as sole product, a *dihydrocodeine*, m. p. 112–114°, *hydrochloride*, m. p. 256° (cf. Mannich and Löwenheim, A., 1921, i, 121; Freund, Melber, and Schlesinger, A., 1920, i, 757). Its methiodide is converted by boiling for a short time with 10% sodium hydroxide solution into *methylidihydromorphimethine* (*de-N-methylidihydrocodeine*), an oil, *hydrochloride*, m. p. 133°, *methiodide*, m. p. 160° (cf. Vongerichten, A., 1899, i, 551; Freund, Melber, and Schlesinger, *loc. cit.*). The reduction of methylmorphimethine, or of either of its dihydroderivatives, by means of palladium-hydrogen in alcoholic solution gives methyltetrahydromorphimethine, *hydrochloride*, m. p. 226°.

[With E. WASER.]—Morphothebaine hydrobromide is converted by heating at 170° with hydrobromic acid in an atmosphere of carbon dioxide, into 6-hydroxyapomorphine, *hydrobromide*, small, colourless needles, m. p. 261–262° (decomp.). The aqueous solution of the salt is coloured reddish-brown by the addition of ferric chloride or of concentrated nitric acid; it immediately reduces silver nitrate. Solutions of the free base in alkali rapidly darken on exposure to the air. W. S. N.

**On the Alkaloids of *Sinomenium acutum*, Rehd. et Wils., *Sinomenine* and *Diversine*.** I. HEIZABURO KONDO, EIJI OCHIAI, and TOMOICHI NAKAJIMA (*J. Pharm. Soc. Japan*, 1923, No. 497, 511–524).—With alcohol and other suitable reagents, two alkaloids, *sinomenine* and *diversine*, have been isolated from *Sinomenium acutum*. *Sinomenine*,  $C_{15}H_{23}O_4N$  or  $C_{15}H_{21}O_4N$ , forms

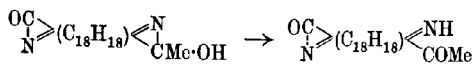
radiating groups of white crystals; it has m. p.  $161^{\circ}$ , on further heating, it becomes crystalline and again melts at  $182^{\circ}$ ,  $[\alpha]_D^{25} -70.76^{\circ}$ ; the *hydrochloride*,  $(2H_2O)$ , forms prisms, m. p.  $231^{\circ}$ , and has  $[\alpha]_D^{25} -82.4^{\circ}$  (anhydrous). Sinomenine has strong reducing power and precipitates silver and gold from their salts. It is soluble in sodium hydroxide solution, and gives a greenish-blue coloration with ferric chloride. It contains two methoxyl and one *N*-methyl groups; and yields a *methiodide*, colourless prisms, m. p.  $251^{\circ}$ . The *monobenzoyl* compound forms colourless prisms, m. p.  $225^{\circ}$  (*chloroaurate* decomposes at  $178^{\circ}$ ); the *monomethyl* compound forms needles, m. p.  $175^{\circ}$  (*hydrochloride*, short prisms, decomposes at  $252^{\circ}$ ).

*Diversine*,  $C_{20}H_{27}O_5N$ , is yellow and amorphous, m. p.  $80-93^{\circ}$ ,  $[\alpha]_D^{25} +6.98^{\circ}$ . It is more strongly reducing than sinomenine and precipitates metallic gold and platinum from their salts; it gives a dark brown coloration with ferric chloride. The *hydrochloride*,  $C_{20}H_{27}O_5N.HCl$ , a yellow, amorphous substance, decomposes at  $135-140^{\circ}$ . *Diversine* contains two methoxyl and one *N*-methyl groups, and gives a *methiodide*,  $C_{20}H_{27}O_5N.MeI$ , a slightly coloured, amorphous compound. When heated with benzoic anhydride, it gives a mixture of mono- and di-benzoyl compounds.

K. K.

**Strychnine and isoStrychnine.** II. E. OLIVERI-MANDALÀ and G. COMELLA (*Gazzetta*, 1923, 53, 619-628).—Oxidation of strychnine by means of permanganate yields the acid obtained by Leuchs (A., 1908, i, 563), together with a second acid which is a product of more advanced degradation of the strychnine molecule, and forms a calcium salt yielding indole on dry distillation (cf. this vol., i, 702). The second acid is amorphous and unstable, and gives analytical results which do not accord with any formula. Oxidation of bromostychnine oxide under similar conditions yields, first, a crystallisable acid, whereas more profound decomposition of the molecule results in the formation only of amorphous products which readily resinify and respond to the reactions for pyrrole.

Further evidence is adduced in support of the view that the passage of strychnine into the isomeric *isostrychnine* may be represented by the scheme



strychnine is not affected by the Grignard reagent, whereas *isostrychnine*, if dried at  $105^{\circ}$ , reacts with excess of magnesium ethyl romide, giving 1 mol. of ethane per mol. of the base; this behaviour is in accord with the presence of a secondary nitrogen atom in the *isostrychnine* molecule. That the latter contains a nitrogen atom with a function different from that of the nitrogen in strychnine is shown by the fact that the normal base, by virtue of its tertiary nitrogen atom, reacts with hydrogen peroxide, giving

the corresponding amino-oxide,  $\text{OC} \begin{smallmatrix} \diagup \\ \text{N} \end{smallmatrix} > (\text{C}_{20}\text{H}_{21}\text{O})\text{:N}\text{:O}$ , whereas the *iso*-base remains unaltered. That *isostrychnine* contains a ketonic group is shown by its ready reaction with semicarbazide.

According to Perkin and Robinson's formula for strychnine (T., 1910, 97, 305), the optical activity of this base is due to the carbon atom which determines the secondary alcoholic function, but the authors regard the activity as caused by the grouping  $>\text{CMe}\cdot\text{OH}$ . Since the latter changes into  $\cdot\text{CMe}$  in *isostrychnine*, this should be optically inactive. Of a number of preparations of *isostrychnine* examined, some were inactive, but others exhibited traces of activity, possibly owing to the presence of impurity.

The amorphous acid obtained by oxidation of strychnine oxide decomposes carbonates and blackens, without melting, at about  $200^\circ$ . Two preparations, dried at  $105^\circ$ , gave C, 52.39, 52.62; H, 4.12, 3.90; N, 5.58, 6.13.

*Bromostrychnine oxide*,  $\text{NO}\text{:C}_{20}\text{H}_{21}\text{OBr} \begin{smallmatrix} \diagup \\ \text{N} \end{smallmatrix} \text{CO} \cdot 3\text{H}_2\text{O}$ , forms groups of large, hard prisms, m. p.  $175^\circ$  (decomp.). Its *hydrobromide*,  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}\cdot\text{HBr}$ , decomposes above  $300^\circ$ , and its *picrate* forms yellow needles. It gives all the reactions of amino-oxides, and by bromine water is reduced to bromostrychnine with liberation of oxygen.

The *acid*,  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}$ , obtained on oxidation of bromostrychnine oxide by means of permanganate, does not melt at  $300^\circ$ , and appears to contain intact the fundamental nucleus of strychnine, as it answers to certain of the colour reactions characteristic of the base.

The dissociation constant of *isostrychnine* is  $0.53 \times 10^{-11}$  at  $25^\circ$ , and for two preparations the specific rotation is found to be  $[\alpha]_D^{25} + 7.27^\circ$  and  $[\alpha]_D^{25} + 6.28^\circ$ .

*Bromoisostrychnine*,  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}\cdot\text{H}_2\text{O}$ , is obtained as an amorphous, white powder which blackens, without melting, at about  $300^\circ$ . It is not soluble in alkali carbonate or hydroxide solution, so that the molecule of water, which is lost at  $105^\circ$ , has not converted the group  $\cdot\text{CO}\cdot\text{N}\cdot$  into  $\text{NH}+\text{CO}_2\text{H}$ ; with *isostrychnine* itself, conversion into *isostrychnic acid* is effected only by heating with sodium ethoxide.

*isoStrychnine semicarbazone*,  $\text{C}_{21}\text{H}_{22}\text{ON}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises in needles, m. p.  $215^\circ$  (decomp.). T. H. P.

**Yohimbine (Quebrachine). III. Esterification of Yohimbic Acid.** ELLEN FIELD (T., 1923, 123, 3003—3006).

**2-Pyrrolidylcarbinol.** N. J. PUTOCHIN (Ber., 1923, 56, [B], 2216—2217). — *2-Pyrrolidylcarbinol*,  $\text{NH} \begin{smallmatrix} \diagup \\ \text{CH}_2 \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2 \end{smallmatrix}$ , a colourless, viscous, unpleasant smelling liquid, b. p.  $148\text{--}153^\circ/12\text{ mm.}$ , is prepared in 40% yield by the reduction of proline ethyl ester by sodium in the presence of ethyl alcohol; the *chloroplatinide*,  $(\text{C}_5\text{H}_{11}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$ , orange-yellow crystals, m. p.  $204^\circ$  (decomp.)

after darkening at 192°, and the *chloroaurate*, m. p. 152°, are described.

H. W.

**Synthesis of Proline.** N. J. PUTSCHIN (*Ber.*, 1923, 56, [B], 2213—2216).—The synthesis of proline has been accomplished in accordance with the scheme:  $\text{NH}_2\cdot\text{CNa}(\text{CO}_2\text{Et})_2 + \text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)(\text{CO}_2\text{Et})_2 \rightarrow \begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\text{-NH} \end{matrix} > \text{C}(\text{CO}_2\text{Et})_2 \rightarrow \begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\text{-NH} \end{matrix} > \text{CH}\cdot\text{CO}_2\text{Et}$ . The yield is about 25% of that theoretically possible.

Ethyl oximinomalonate, b. p. 172°/12 mm., is reduced to ethyl aminomalonate (hydrochloride, m. p. 162°) by the action of aluminium amalgam in the presence of moist ether or catalytically in the presence of spongy platinum. The ester hydrochloride is converted by sodium ethoxide and trimethylene bromide in alcoholic solution and subsequent treatment of the product with concentrated hydrochloric acid into proline, m. p. 205°, which is isolated through its copper salt.

H. W.

**Complex Thiocyanates of Tervalent Elements. II.** G. SCAGLIARINI and G. TARTARINI (*Gazzetta*, 1923, 53, 617—619; cf. this vol., i, 547).—By means of the method previously employed, degradation products of chromithiocyanates intermediate between  $(\text{NH}_4)_3[\text{Cr}(\text{SCN})_6]$  and  $\text{Cr}(\text{SCN})_3$  have been obtained, use being made of piperidine and piperazine to fix the decomposition products of the ion  $\text{Cr}(\text{SCN})_6^{3-}$ .

*Piperidine chromihexathiocyanate*,  $(\text{C}_5\text{H}_{11}\text{N},\text{H})_3[\text{Cr}(\text{SCN})_6]$ , forms pale violet, cubical crystals; *piperidine aquochromipentathiocyanate*,  $(\text{C}_5\text{H}_{11}\text{N},\text{H})_2[\text{Cr}(\text{SCN})_5(\text{OH}_2)]\cdot\text{H}_2\text{O}$ , violet, prismatic plates; *piperazine aquochromipentathiocyanate*,  $(\text{C}_4\text{H}_{10}\text{N}_2,\text{H})_2[\text{Cr}(\text{SCN})_5(\text{OH}_2)]\cdot\text{H}_2\text{O}$ , violet, cubical crystals, and *piperazine aquochromitetrahiocyanate*,  $(\text{C}_4\text{H}_{10}\text{N}_2,\text{H})_2[\text{Cr}(\text{SCN})_4(\text{OH})(\text{OH}_2)]$ , violet needles.

T. H. P.

**The Structure of Apophyllenic Acid.** ALFRED KIRPAL and EWALD REITER (*Annalen*, 1923, 433, 112—116).—Mumm and Gottschaldt (*A.*, 1922, i, 862) found that, by the action of silver oxide on the methiodide of 3-methyl 4-ethyl 2:6-dimethylcinchoneronate, it is the 4-carbethoxyl, and not the 3-carbomethoxyl, group which is attacked. 2:6-Dimethylapophyllenic acid was accordingly described as a 4-betaine, and its formation was ascribed to the greater ease of formation of a 4-betaine ring. An alternative explanation is that the 3-carbomethoxyl group is prevented by the 2-methyl group (steric hindrance) from undergoing the reaction, and that otherwise a 3-betaine would be formed. This is certainly borne out by the production, by the action of silver oxide on 3-methyl 4-ethyl cinchoneronate methiodide (prisms, decomp. 170°), of a greater quantity of the 4-ethyl ester of cinchoneronic acid methylbetaine than of the 3-methyl ester. Any difference in ease of hydrolysis of the ester groups is due to position, and not to difference in their alkyl groups, because a similar result attends

the use of *dimethyl cinchomerona methiodide* (pale yellow needles, decomp. 157°), the 4-methyl ester preponderating in the product. The alkaline half-hydrolysis of neutral cinchomeronic ester gives almost exclusively the 3-ester. Similar behaviour might have been expected in hydrolysing the above methiodides; but the actual results, being different, must be attributed to the tendency to formation of a 3-betaine. A 3-betaine formula for apophyllenic acid is held to be reconcilable with Pfeiffer's views on the structure of betaines (A., 1922, i, 720) (cf. Mumm and Gottschaldt, *loc. cit.*).

The same ester is formed by the action of diazomethane on apophyllenic acid as by the action of methyl iodide on its silver salt.  
W. S. N.

**Supposed Cases of Isomerism in the Isatin Series.** A. HANTZSCH (*Ber.*, 1923, 56, [B], 2110—2119).—A further communication in the controversy between Hantzsch and Heller concerning the existence of isomerides in the isatin series (cf. Heller, A., 1920, i, 766; 1921, i, 891; Heller and Benade, A., 1922, i, 582; Hantzsch, A., 1921, i, 597; 1922, i, 1177).

The supposed isomerides in the isatin series do not exist. The isomerides described by Heller are either not homogeneous (dimethylisatin III or the isomeric dimethylisatin silver), do not correspond with the empirical formula of isatin (dimethylisatin IV), or are true polymeric, generally dimeric, compounds, as in the case of most of the other supposed isomerides. In connexion with the differences in colour of the silver salts obtained in the isatin series by different workers, it is pointed out that it is well established that such discordances can exist in the colour of solid compounds and particularly in deeply coloured silver salts, but that such differences are quite unimportant. Dimethylisatin silver has been considered by Heller to be a *N*-silver salt because of its grey colour (in contrast with the customary silver salts) and of the impossibility of converting it into the corresponding methyl ether. All these silver salts, which are characterised by their smooth conversion into *O*-alkyl ethers and, as now shown, by their primary transformation into *O*-acyl derivatives, have been considered by Heller to be *N*-salts chiefly because isatindianil which is free from oxygen gives a silver salt and a similar compound cannot be obtained from the supposed dimethylisatin lactim; the author considers that the salt formation from the dianil has no bearing on the conception of the isatin salts, and brings forward evidence to prove that dimethylisatin lactim does not exist.

Dimethylisatin silver, which in the pure state is bordeaux-red like the other silver salts, and not grey as described by Heller, is converted by pure benzoyl chloride in the presence of anhydrous ether and absence of moisture at the atmospheric temperature into *dimethylisatin O-benzoate*,  $C_6H_2Me_2 < \begin{smallmatrix} CO \\ -N \end{smallmatrix} > C \cdot OBz$ , large, blood-red crystals, m. p. 118—119°; it is hydrolysed by sodium hydroxide solution into dimethylisatin and benzoic acid. If the reagents are not completely pure and dry, the reaction between the silver salt

and benzoyl chloride leads to the production of much regenerated dimethylisatin and tetramethylisatoid (annexed formula) which has been described by Heller as dimethylisatinlactim. It has m. p. 204—205° (decomp.). Its isatoid structure is deduced from determinations of its molecular weight in benzene and camphor and from the similarity of its absorption spectrum when dissolved in chloroform with that of tetramethylisatoid monomethyl ether and its dissimilarity from dimethylisatin *O*-methyl ether. It dissolves in aqueous alkali, giving a bluish-red solution of the salt, from which it is precipitated unchanged by immediate, exact neutralisation with acid. If, however, an excess of acid is used, the precipitate is not homogeneous; such mixtures have been described by Heller as "dimethylisatol." They consist in part of tetramethylisatoid anhydride,  $C_{20}H_{16}O_6N_2$  (Heller's dimethylisatin IV), m. p. 297—300°, which is conveniently prepared by treating tetramethylisatoid with boiling glacial acetic acid. The action of glacial acetic acid and acetic anhydride on tetramethylisatoid gives a very stable, pale yellow product, m. p. 243°, which appears to be an acetyl derivative.

H. W.

#### The Preparation of Homologues of Isatin : Preparation of 7-Bromo-5-methylisatin. (MILLE) MARCELLE RESSY and

ANDRÉI P. ORTODOCSE (*Bull. Soc. chim.*, 1923, [iv], **33**, 1297—1299).

—The preparation was effected by a method similar to that used in the case of the isomeride (this vol., i, 833). Acetylation and subsequent bromination of *p*-toluidine yielded aceto-*o*-bromo-*p*-toluidide. The corresponding benzoyl derivative was also prepared. Hydrolysis of either of these substances by means of alcoholic potassium hydroxide resulted in the formation of *o*-bromo-*p*-toluidine. Condensation of the hydrochloride of this base with hydroxylamine hydrochloride and chloral hydrate gave the di-bromodi-*p*-tolylamidine of the oxime of glyoxalic acid from which oximinobromoaceto-*p*-toluidide is obtained on hydrolysis. The last-named substance in solution in boiling sulphuric acid yields, on being added to water, orange-red prismatic needles of 7-bromo-5-methylisatin, m. p. 180°. The oxime has m. p. 230° and the phenylhydrazone 242°. The substance is stated to possess greater tinctorial power than its isomeride. Benzoyl-*o*-bromo-*p*-toluidide, m. p. 125°, forms lustrous needles which have in appearance some resemblance to boric acid.

H. J. E.

#### The Action of Sulphur on Organic Compounds. VII. Quinoline and Sulphur. LUDWIK SZPERL and TADEUSZ W.

BEZIERSKI (*Roczniki Chemji*, 1923, **3**, 177—183; cf. this vol., i, 1191).

—Quinoline was heated at 220—235° with sulphur in molecular proportions for 185 hours in an atmosphere of carbon dioxide. After removing the unchanged quinoline, the solid residue was found to consist of two compounds which were separated, after being purified by sublimation, by means of boiling benzene. The soluble compound,  $C_{10}H_7NS$ , obtained in very small amount, formed fine, pale yellow

needles, m. p. 249—251°; it forms an orange *picrate*, m. p. 258—261°, and a *sulphate* carbonising at 270°. The compound insoluble in benzene crystallises from acetic acid, melts at 305—305.5°, and forms a red *picrate*, m. p. 278—279°; the *sulphate* forms golden-yellow crystals which become red on keeping. The compound is thus identical with Edinger and Lubberger's thioquinanthrene (A., 1897, i, 204). It is suggested that the original formula,  $(C_9H_5NS)_n$ , is correct, and not that proposed later by Edinger and Ekeley (A., 1902, i, 230). Oxidation of the compound with nitric acid gives nicotinic acid.

G. A. R. K.

#### Internal Metallic Complexes of the Hydroxyquinolines.

G. BARGELLINI and I. BELLUCCI (*Gazzetta*, 1923, 53, 605—616).—According to Noeltig and Trautmann (A., 1891, 325), Kostanecki (A., 1891, 579), and Möhlau and Steimmig (*Z. Farb. Text. Chem.*, 1904, 3, 358), only those hydroxyquinolines with the hydroxyl group in the 8-position are able to function as mordant colouring matters. The mordant dyeing properties of chemical compounds are considered by Werner and Thomann (A., 1908, i, 440) to depend on the capacity to form co-ordinated complex salts, and this view is supported by much direct experimental evidence.

Metallic derivatives of 8-hydroxyquinoline have been prepared by Skraup (A., 1883, 92) and by Fox (T., 1910, 97, 1119), and the authors now describe the nickel and palladium compounds. With concentrated potassium chloroplatinate solution, 8-hydroxyquinoline in acetic acid solution yields a red, crystalline precipitate which sublimes under reduced pressure; with cobalt acetate, it gives a brownish-yellow coloration, and with ferrous sulphate a reddish-brown precipitate which undergoes rapid alteration in the air. The ability to form internal metallic complexes and hence lakes is not influenced by replacing the hydrogen atoms of 8-hydroxyquinoline by other atoms or groups, since copper, nickel, palladium, and ferrous salts are formed by 5:7-dibromo-8-hydroxyquinoline (cf. Bedall and Fischer, A., 1881, 613) and by hydroxymethyl-8-hydroxyquinoline (cf. Manasse, A., 1903, i, 28; Cohn, A., 1911, i, 567). Hydroxyquinolines with the hydroxyl in positions other than the 8-position are incapable of yielding internal metallic complexes.

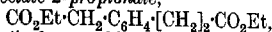
The *nickel* compound of 8-hydroxyquinoline,  $(C_9H_4ON)_2Ni$ , forms a greenish-yellow, pulverulent precipitate, and is highly stable towards heat or reagents. It decomposes on prolonged heating at 350—400°, and sublimes unchanged as a greenish-yellow, microcrystalline deposit when heated at 300° either under reduced pressure or in a current of carbon dioxide. The *palladium* compound,  $(C_9H_4ON)_2Pd$ , forms a canary-yellow, microcrystalline precipitate, sublimes at about 300°, and decomposes at about 400°.

T. H. P.

**Decahydroisoquinoline.** LOUIS HELFER (*Helv. Chim. Acta*, 1923, 6, 785—799).—Decahydroisoquinoline cannot be prepared by hydrogenation of isoquinoline, and attempts to prepare it from  $\beta$ -cyclohexylethylamine or its derivatives by the action of methylal were unsuccessful. Success was eventually attained by a method

similar to Ladenburg's piperidine synthesis. The method was first applied to the preparation of tetrahydroisoquinoline. From homo-*o*-phenylenediacetic [phenylene-1-acetic-2-propionic] acid (Einhorn and Lumsden, A., 1896, i, 45) homo-*o*-xylylenediamine [1-aminomethyl-2-β-aminoethylbenzene] was prepared, through the ethyl ester, hydrazide, azide, and urethane. Distillation of the hydrochloride of the diamine gave tetrahydroisoquinoline. In a similar manner, distillation of the corresponding hexahydro-diamine hydrochloride, obtained from hexahydrophenylene-1-acetic-2-propionic acid, gave decahydroisoquinoline.

*Ethyl phenylene-1-acetate-2-propionate,*



is a nearly colourless oil of agreeable odour, b. p. 198—199°/16 mm. By hydrazine hydroxide at 125—130° this is converted into *o*-phenylene-acetopropionohydrazide, white, silky needles, m. p. 170—171°. Nitrous acid converts this into the corresponding *azide*, a yellow oil which was not isolated, but was converted directly into the *urethane*,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , white needles, m. p. 81°. When this is heated under pressure at 120—130° with hydrochloric acid, it gives the hydrochloride of the diamine. 1-Aminomethyl-2-β-aminoethylbenzene is a colourless oil with a strong basic odour, b. p. 268—270°/735 mm.; when exposed to air it forms a white, crystalline *carbonate*; its *hydrochloride* forms fine needles, m. p. 258°, and the *picrate*, small, yellow needles, m. p. 224°.

Hydrogenation of phenylene-1-acetic-2-propionic acid proceeds smoothly when the substance is pure and a highly active platinum black is used. cycloHexane-1-acetic-2-propionic acid crystallises in small needles, m. p. 106—107°. It is distinguished from the non-hydrogenated acid by its lower solubility in water and complete solubility in cold benzene. The *ethyl* ester is a colourless oil, b. p. 191—192°/15 mm.; the *hydrazide*, which is difficult to crystallise, has m. p. 176°; the *urethane* obtained from the hydrazide is a viscous, colourless oil which could not be crystallised. 1-Amino-methyl-2-β-aminoethylcyclohexane is a strong base; it forms an oil, b. p. 254—255°/731 mm.; its *hydrochloride* is a white salt which liquefies in moist air, and the *picrate* crystallises in yellow needles, m. p. 105°. Decahydroisoquinoline is a strongly basic, colourless oil, b. p. 208—209°/730 mm., distinguished from tetrahydroisoquinoline by its more penetrating odour and by the fact that it does not reduce ammoniacal silver nitrate. The *hydrochloride* crystallises in spangles, m. p. 176°; *picrate*, small, yellow needles, m. p. 144—145°; *chloroplatinate*, small crystals, m. p. 201° (decomp.).

E. H. R.

*ω*-Trichloro- and *ω*-Tribromo-quinaldine and the Preparation of Quinaldinic Acid. DALZIEL LLEWELLYN HAMMICK (T., 1923, 123, 2882—2884).

Alkylation and Aralkylation of Carbazole. NATIONAL ANILINE AND CHEMICAL CO., INC. (Brit. Pat. 192376).—Direct alkylation is effected by the interaction of carbazole and alkylating agents, in the presence of a dehydrating or condensing agent (e.g., alkali

hydroxides) and, preferably, of an indifferent organic liquid (e. g., toluene). [Cf. *J.S.C.I.*, 1923, Dec.] W. T. K. B.

**The Solubility of the Phenylenediamines and of their Monoacetyl Derivatives.** NEVIL VINCENT SIDGWICK and JAMES ACHESON NEILL (T., 1923, 123, 2813—2819).

**The Basic Derivatives of the Ethylbenzene Series.** JULIUS VON BRAUN and GEORG BLESSING (*Ber.*, 1923, 56, [B], 2153—2161).—It has been established that the  $\beta$ -nitrophenylethyl chloride, m. p. 48—49°, prepared from  $\beta$ -phenylethyl alcohol is entirely the para-derivative. The reactions of  $\beta$ -*p*-aminophenylethylamine have been examined in detail.

Bisphenylethylamine is converted into its benzoyl derivative, m. p. 61°, which is transformed by fuming nitric acid into the corresponding dinitro-compound,  $C_{23}H_{21}O_5N_3$ , lustrous, pale-yellow leaflets, m. p. 152°. The latter substance is converted by treatment with phosphorus pentachloride and subsequent distillation under diminished pressure into benzonitrile and  $\beta$ -*p*-nitrophenylethyl chloride, m. p. 49°, which is identical with the product obtained from  $\beta$ -phenylethyl chloride. Since it is improbable that the compounds obtained by two widely differing methods would be contaminated to the same degree by the presence of an isomeride they are to be regarded as the pure para-derivative.

*p*-Nitrophenylacetonitrile dissolved in tetrahydronaphthalene is converted by hydrogen in the presence of a nickel catalyst at 120° into *p*-aminophenylacetonitrile, m. p. 45—46°, the yield attaining 70% of that theoretically possible; the hydrochloride, m. p. 217—220°, and the *picrate*, m. p. 185°, are described. If reduction is effected at 130° the cyano-group is also attacked with the production of the corresponding primary and secondary amines.  $\beta$ -*p*-Aminophenylethylamine,  $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2$ , is a colourless liquid, b. p. 140—142°/12 mm.; the dihydrochloride, m. p. 270—280°, the *dipicrate*, orange-coloured needles, decomp. 205—210°, the *dibenzoyl* derivative, m. p. 223°, the *diacetyl* compound, m. p. 190—192°, and the *diphenylthiocarbamide*, m. p. 166—167°, are described. The hydrochloride of the base is readily converted by a molecular proportion of sodium nitrite into tyramine,  $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2$ , m. p. 159—161°, the yield being 80% of that theoretically possible. Bis- $\beta$ -*p*-aminophenylethylamine,  $(NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2)_2NH$ , is a viscous liquid, b. p. 200—220°/1—2 mm.; the trihydrochloride, m. p. 270—275° (decomp.), the *tripicrate*, m. p. 135—140°, the *triacetyl* compound, m. p. 189—191°, and the *dibenzoyl* derivative, m. p. 270—280°, are described. The triamine is converted by two molecular proportions of nitrous acid into bis- $\beta$ -*p*-hydroxyphenylethylamine (see later).

*p*-Hydroxyphenylacetonitrile is hydrogenated in tetrahydronaphthalene solution at 120—130° to a mixture of  $\beta$ -*p*-hydroxyphenylethylamine and bis- $\beta$ -*p*-hydroxyphenylethylamine. The latter substance forms colourless crystals, m. p. 194°. In comparison with the corresponding primary amine, it is very slightly active pharmaco-

logically. The *hydrochloride*, m. p. 220°, the *sulphate*, the non-crystalline *acetyl* derivative, and the *tribenzoyl* compound, m. p. 102°, are described. Catalytic reduction of *p*-hydroxyphenylacetonitrile dissolved in cyclohexanol at 120–130° leads to the production of a mixture of the three theoretically possible bases in which cyclohexyl- $\beta$ -*p*-hydroxyphenylethylamine,  $C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OH$ , predominates. It crystallises in aggregates of needles, m. p. 94°, b. p. 220–223°/15 mm.; the *hydrochloride*, m. p. 258–260°, the *sulphate*, the *picrate*, m. p. 198°, and the *dibenzoyl* derivative, m. p. 137°, are described. In a similar manner, cyclohexyl- $\beta$ -*p*-aminophenylethylamine, a pale yellow, somewhat viscous liquid, b. p. 160°/1 mm., is obtained in 40–45% yield by the reduction of *p*-aminophenylacetonitrile dissolved in cyclohexanol. The *dihydrochloride*, the *monopicate*, m. p. 147°, the *diacetyl* compound, m. p. 129°, the *dibenzoyl* derivative, m. p. 140°, and the diquaternary iodide,  $C_{19}H_{24}N_2I_2$ , m. p. 186–188°, are described.

The complete methylation of *p*-aminophenylethylamine to the compound  $NMe_3I \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_3I$  appears to be attended by considerable and unexplained uncertainties, so that it is preferable to start from  $\beta$ -*p*-dimethylaminophenylethylamine. For this purpose, *p*-aminophenylacetonitrile is converted successively into the quaternary iodide,  $CN \cdot CH_2 \cdot C_6H_4 \cdot NMe_3I$ , orange-coloured needles, m. p. 177°, and *p*-dimethylaminophenylacetonitrile, b. p. 162–165°/11 mm., m. p. 55–56° (*hydrochloride*, m. p. 162°; *picrate*, m. p. 127°). The nitrile is reduced by sodium and alcohol to  $\beta$ -*p*-dimethylaminophenylethylamine, a colourless liquid, b. p. 120–125°/11 mm. (the non-crystalline *hydrochloride* and the *picrate*, m. p. 133–135°, are described). The new base is converted into the corresponding diquaternary iodide, colourless crystals which do not melt below 300°, from which *p*-dimethylaminovinylbenzene,  $NMe_3 \cdot C_6H_4 \cdot CH \cdot CH_2$ , is prepared; it is a colourless liquid, b. p. 90–91°/vacuum, which does not appear to become appreciably polymerised when preserved. The non-crystalline *hydrochloride*, the *chloroplatinate*, m. p. 150°, and the *picrate*, yellow leaflets, m. p. 120–121°, are described. H. W.

**3-Amino- and 3-Hydroxy-quinolines.** G. BARGELLINI and M. SETTIMI (*Gazzetta*, 1923, 53, 601–605).—The authors have attempted to prepare 3-hydroxyquinoline and 3-aminoquinoline by the general methods previously described (this vol., i, 482, 847), but without success in either case. The interaction of *o*-aminobenzaldehyde and chloroacetaldehyde in presence of potassium hydroxide yields no trace of 3-hydroxyquinoline, probably owing to resinification of the aldehyde. Potassio-phthalimide could not be induced to condense with either chloroacetaldehyde or chloroacetal to form phthalimidooacetaldehyde, so that condensation of the latter with *o*-aminobenzaldehyde to 3-aminoquinoline could not be effected.

3-Aminoquinoline may, however, be readily prepared by the reduction, by means of stannous chloride and hydrochloric acid, of 3-nitroquinoline, which is easily obtainable from *o*-aminobenzaldehyde and methazonic acid (cf. Badische Anilin- & Soda-Fabrik,

A., 1921, i, 517). Treatment of 3-aminoquinoline with nitrous acid gives 3-hydroxyquinoline. These methods may be used with advantage in place of the tedious methods of preparing these compounds described by Mills and Watson (T., 1910, 97, 741).

3-Hydroxyquinoline picrate forms yellow crystals, m. p. 240—245° (decomp.). T. H. P.

**Synthesis of some Pyridylpyrroles.** J. P. WIBAUT and ELISABETH DINGEMANSE (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 426—435).—An account of preliminary work in connexion with an attempted synthesis of an isomeride of nicotine. By heating 2-aminopyridine with mucic acid at 140°, 1-(2'-pyridyl)pyrrole is obtained as a white, crystalline compound, m. p. 17°, b. p. 140—145°/15 mm., and 260—261°/760 mm., which gives a *picrate*, m. p. 143°, and a *methiodide*, m. p. 141—142°. When 1-(2'-pyridyl)pyrrole is passed over pumice heated at 670—690°, two isomeric C-(2'-pyridyl)pyrroles are formed, one of which is non-volatile in steam, and melts at 132.5°. The other is volatile in steam, melts at 90°, and gives a *picrate*, m. p. 227—228°, and a *methiodide*, m. p. 148°. When the latter isomeride is treated with potassium, and the potassium derivative is heated in a sealed tube with methyl iodide at 100°, C-(2'-pyridyl)-1-methylpyrrole *methiodide*, m. p. 186°, is obtained, from which the free base is liberated by distillation with lime. C-(2'-Pyridyl)-1-methylpyrrole *picrate* was found to melt at 143°. H. H.

**Synthesis of some  $\alpha$ -Pyridylpyrroles and a Second Isomer of Nicotyrin.** J. P. WIBAUT and ELISABETH DINGEMANSE (*Rec. trav. chim.*, 1923, 42, 1033—1049).—A fuller account of work already abstracted (preceding abstract). The following details are new. Dry hydrogen chloride reacts with an ethereal solution of 1-(2'-pyridyl)pyrrole to give its *hydrochloride*, a greyish-white powder, m. p. 152°, but the pyrrole liberated by the action of alkali on this salt gives a *picrate*, m. p. 180°, which is not identical with that formed directly. 2-Aminopyridine *mucate* melts at 174° (decomp.), but the reaction between ethyl *mucate* and 2-aminopyridine at 105° yields the *diamide* of *diaminopyridylmucic acid*, m. p. 202°. The *picrate* of C-(2'-pyridyl)pyrrole of m. p. 90° is now stated to melt at 222—223° instead of 227—228°. The *hydrochloride* of this C-(2'-pyridyl)pyrrole melts at 179°. The *picrate* (m. p. 211°) and *methiodide* (m. p. 167°) of the isomeric C-(2'-pyridyl)pyrrole, m. p. 132°, are now described. The isomeric bases C-(2-pyridyl)-1-methylpyrrole, isomeric with nicotyrine, are described. That from C-(2'-pyridyl)pyrrole, m. p. 90°, boils at 273°/764 mm., and gives the *methiodide* and *picrate* previously described. That from C-(2'-pyridyl)pyrrole, m. p. 132°, gives a *picrate*, m. p. 197—198°. H. H.

**The Additive Formation of Four-membered Rings. II. The Conditions which confer Stability on the Dimethine-diazidines.** CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (T., 1923, 123, 2745—2752).

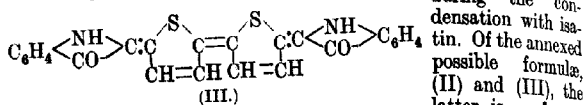
**New Investigations with Diazomethane; Alloxantin.**

HEINRICH BULTZ and HANS PAETZOLD (*Annalen*, 1923, 433, 64—87).—The determination of the constitution of alloxantin is rendered difficult by the ease with which it dissociates into alloxan and dialuric acid; even in a saturated aqueous solution, dissociation proceeds to as much as 80% (Büllmann and Bentzon, A., 1918, i, 352). Since methylation may be effected in the absence of water by the use of diazomethane, it was hoped that by means of that reagent the structure of alloxantin might be elucidated. But even in the complete absence of water, the products of the action of diazomethane on alloxantin are derived from alloxan and dialuric acid; consequently, the results obtained only contribute to the constitutional problem by providing a further illustration of the ease of dissociation of alloxantin.

Actually it is immaterial whether alloxantin or tetramethylalloxantin is used, and whether water of crystallisation is present or not; the products are 5:6-methylenedioxy-1:3-dimethyluracil,  $\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{O} > \text{CH}_2$  (I), large, flat, rhombic leaflets (possibly monoclinic), m. p. 170°, and 5:6-dimethoxy-1:3-dimethyluracil,  $\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{OMe}$  (II), slender prisms (apparently monoclinic), m. p. 59°. The compound (I), which has already been obtained as a syrup (Herzig, A., 1922, i, 373), is also produced by the action of diazomethane on alloxan monohydrate, dimethylalloxan monohydrate, or anhydrous dimethylalloxan, but the last named reacts fully only in the presence of water. The dimethoxy-derivative (II) is also obtained by the action of diazomethane on dialuric acid or 1:3-dimethyldialuric acid.

The constitution of the methylene ether (I) follows from its mode of formation and properties. It is unaffected by treatment with concentrated nitric acid, with alcoholic sodium ethoxide, or, in glacial acetic acid solution, with hydrogen peroxide or with sodium amalgam. The ether is dissolved by means of alkali hydroxide solution, but is evidently changed, since it is not recovered by acidifying the solution. The methylenedioxy-ring is broken by the action of cold, or, more rapidly, by means of boiling, water, or by the action of hot, concentrated hydrochloric acid. In the first reaction, formaldehyde is produced; the second leads to the formation of the 6-chloromethyl ether of 1:3-dimethylisodialuric acid,  $\text{NMe}\cdot\text{CO}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CH}\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ , long prisms, m. p. 92° (corr.), anhydrous, or with  $\text{H}_2\text{O}$ , long prisms, m. p. 88° (corr.). The chloromethoxyl group is probably situated at position 6, rather than at 5, since the molecule of water is apparently held about as firmly as in alloxan monohydrate, and is therefore probably attached to the 5-carbonyl group (see below). The action of warm hydriodic acid, *d* 1.46, on the methylene ether gives the 6-iodomethyl ether, m. p. 83°, or with  $\text{H}_2\text{O}$ , short, compact rhombs, m. p. 123° (corr.). This, and the chloromethyl ether, are stable towards acids, but are decomposed

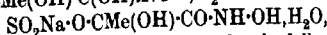
both  $\alpha$ -hydrogen atoms of the thiophen molecule are eliminated during the condensation with isatin. Of the annexed possible formulae, (II) and (III), the latter is preferred,



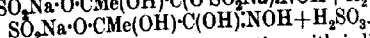
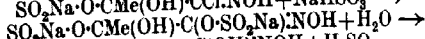
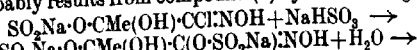
since formula (II) does not account for the intense colour of indophenine. Moreover, either indophenine or mesoxophenine, to which a similar structure is assigned, may be reduced in acetic acid solution by means of zinc dust to a leuco-base, from which the dye is regenerated by making the solution alkaline and shaking in contact with air, this being well expressed by the indigoid structure (III). The direct coupling of two thiophen molecules, as in (III), is actually known to occur, since thiophen is converted into 2:2'-di-thienyl by the action of concentrated sulphuric acid (Töhl, A., 1894, i, 276).

W. S. N.

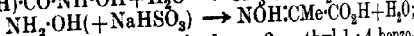
**Hydrogen Sulphite Compounds: Hydroxamic Acids and Derivatives of 1:2:4-Triazole.** C. GASTALDI (Gazzetta, 1923, 53, 635—645).—The action of sodium hydrogen sulphite on chloroximinooacetone yields (1) the sodium sulphite compound of pyruvylhydroximinic chloride, which has been already considered (A., 1922, i, 626), and (2) the sodium sulphite compound of pyruvylhydroxamic acid,  $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{NOH}\cdot\text{H}_2\text{O}$  or



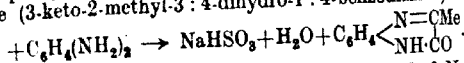
which probably results from compound (1) by the following reactions:



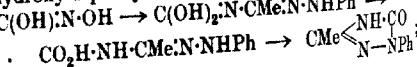
Compound (2) gives the iodoform reaction with iodine and sodium carbonate, and with ferric chloride yields the intense cherry-red coloration characteristic of the hydroxamic acids; when heated with dilute sulphuric acid, it gives the oxime of pyruvic acid,  $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} +$



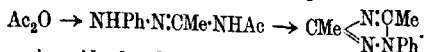
with *o*-phenylenediamine it yields 3-hydroxy-2-methyl-1:4-benzodiazine (3-keto-2-methyl-3:4-dihydro-1:4-benzodiazine):



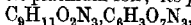
With phenylhydrazine, it gives a compound,  $\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$ , which appears to be a phenylhydrazone of pyruvylhydroxamic acid,  $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , since it may readily be converted into 1:2:4-triazole derivatives. Thus, when this compound or its acetyl derivative is heated, or the latter is treated with sodium ethoxide, 5-hydroxy-1-phenyl-3-methyl-1:2:4-triazole results,  $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH} \rightarrow \text{C}(\text{OH})_2\cdot\text{N}\cdot\text{CMe}\cdot\text{N}\cdot\text{NHPh} \rightarrow$



when, however, the phenylhydrazone is heated with acetic anhydride, 1-phenyl-3:5-dimethyl-1:2:4-triazole is formed,  
 $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{NOH} \xrightarrow{-\text{CO}_2} \text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{NH}_2 +$



*Pyruvylhydroxamic acid phenylhydrazone* forms crystals which, after being dried at 100°, melt and lose carbon dioxide at 178–179°. When reduced in sodium hydroxide solution by means of sodium amalgam, it yields  $\alpha$ -phenylhydrazidopropionic acid, m. p. 172–173° (decomp.) (cf. von Miller and Plöchl, A., 1892, 1196), or if the reduction is effected at 0° two compounds, m. p. 124–125° and 144°, respectively. Its sodium salt forms pale yellow prisms, gives an alkaline aqueous solution, and decomposes gradually in the air or violently when heated on platinum foil; its *picrate*,



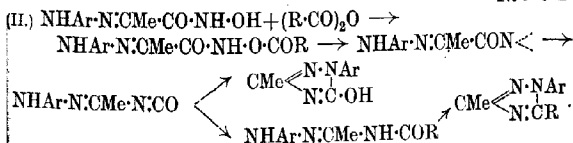
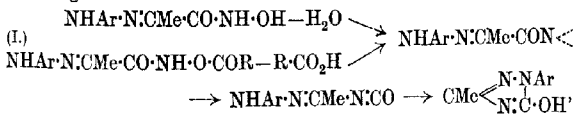
crystallises in red needles, m. p. 158°, and its *acetyl* derivative forms colourless laminae, m. p. 142° (evolution of gas), gives a brick-red coloration with concentrated sulphuric acid and a brownish-yellow coloration with ferric chloride in alcoholic solution, and exhibits normal cryoscopic behaviour in naphthalene and in acetic acid.

*Pyruvylhydroxamic acid phenylmethylhydrazone*,

$\text{NMePh}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$  or  $\text{NMePh}\cdot\text{N}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ , prepared similarly to the phenylhydrazone, forms yellow needles, m. p. 126°, gives a deep red coloration with ferric chloride in aqueous or alcoholic solution, is decomposed by concentrated sulphuric acid, and reduces hot Fehling's solution and cold ammoniacal silver nitrate solution. Its *acetyl* derivative crystallises in golden-yellow needles, m. p. 82–83°, has the normal molecular weight in freezing benzene, reduces ammoniacal silver nitrate solution, and gives a brick-red coloration with concentrated sulphuric acid.  
 T. H. P.

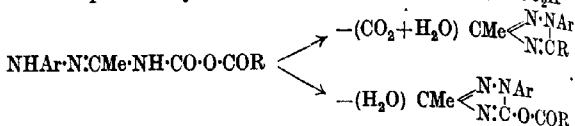
#### Hydroxamic Acids and Derivatives of 1:2:4-Triazole.

C. GASTALDI (*Gazzetta*, 1923, 53, 629–634).—According to the views of Stieglitz (A., 1897, i, 43; 1903, i, 235), the formation of derivatives of 1:2:4-triazole from pyruvylhydroxamic acid arylhydrazones (preceding abstract) may be indicated by the following schemes:



It may be, however, that the carbimide formed unites with a molecule

of the aliphatic acid giving a mixed anhydride from which the two triazole compounds may then result:  $\text{NHAr}\cdot\text{N}\cdot\text{CMe}\cdot\text{N}\cdot\text{CO} + \text{R}\cdot\text{CO}_2\text{H} \rightarrow$



The *propionyl* derivative of *pyruvylhydroxamic acid phenylhydrazone*,  $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{NO}\cdot\text{COEt}$ , prepared from propionic anhydride on pyruvylhydroxamic acid phenylhydrazone, crystallises in colourless laminæ, m. p.  $121^\circ$ , at which temperature it loses propionic acid and yields 5-hydroxy-1-phenyl-3-methyl-1:2:4-triazole, m. p.  $167^\circ$ .

1-Phenyl-3-methyl-5-ethyl-1:2:4-triazole,  $\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{CET}\cdot\text{NPh} \end{smallmatrix}$  prepared, together with the propionyl derivative of 5-hydroxy-1-phenyl-3-methyl-1:2:4-triazole, from propionic anhydride and pyruvylhydroxamic acid phenylhydrazone, forms a dense, colourless liquid, b. p.  $160\text{--}165^\circ/14\text{ mm.}$ ; its *hydrochloride* forms colourless prisms, m. p.  $207^\circ$ , its *chloroplatinate* orange-yellow prisms, m. p.  $190^\circ$ , and its *picrate* bundles of long, yellow laminæ, m. p.  $138^\circ$ .

*Pyruvylhydroxamic acid p-bromophenylhydrazone*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ , obtained by the action of *p*-bromophenylhydrazine on the bisulphite compound of pyruvylhydroxamic acid, crystallises in colourless prisms, m. p.  $185\text{--}186^\circ$ , gives a blood-red coloration with concentrated sulphuric acid, and, in alcoholic solution, yields a violet-blue coloration with ferric chloride. Its *sodium* salt was analysed, and its *acetyl* derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_5\text{N}_3\text{Br}$ , separates in colourless needles, m. p.  $155^\circ$ , and, when heated at its melting point, loses acetic acid and gives 5-hydroxy-1-*p*-bromophenyl-3-methyl-1:2:4-triazole,  $\text{N} \begin{smallmatrix} \text{CMe}=\text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} \end{smallmatrix}$ , which crystallises in colourless needles, m. p.  $267^\circ$ .

1-*p*-Bromophenyl-3:5-dimethyl-1:2:4-triazole,  $\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} \end{smallmatrix}$  obtained, together with the acetyl derivative of 5-hydroxy-1-*p*-bromophenyl-3-methyl-1:2:4-triazole, by boiling a mixture of pyruvylhydroxamic acid *p*-bromophenylhydrazone and acetic anhydride, forms a pale yellow, dense liquid, b. p.  $225\text{--}230^\circ/45\text{ mm.}$ ; its *hydrochloride* is obtained in colourless laminæ, m. p.  $239^\circ$ .

*Pyruvylhydroxamic acid p-nitrophenylhydrazone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ , crystallises in chestnut-red prisms, m. p.  $224^\circ$  (decomp.), dissolves in dilute sodium hydroxide solution to a deep violet-red solution, and in alcoholic solution gives a dark green coloration with ferric chloride. Its *acetyl* derivative forms slender, yellow needles, m. p.  $170^\circ$ , and, when heated at its melting point, gives 5-hydroxy-1-*p*-nitrophenyl-3-methyl-1:2:4-triazole. T. H. P.

**Polypyrroles.** ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 175—179; cf. A., 1922, i, 766).—In accordance with its constitution, Dennstedt's tripyrrole, which is formed of two pyrrole rings united in the 2-position to a pyrrolidine nucleus, yields black compounds only with difficulty, but 2-hydroxydipyrrole gives such compounds even more readily than pyrrole itself. It hence appears probable that more complex pyrrole derivatives will yield black products still more easily. This conclusion is supported by the results now described.

Ethyl  $\beta$ -pyrrolylpropionate,  $\begin{array}{c} \text{CH-CH} \\ | \quad | \\ \text{CH-NH} \end{array} > \text{C-CO-CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , prepared from magnesium pyrrole iodide and ethyl succinate, crystallises in needles, m. p.  $70^\circ$ , and the free acid,  $\text{C}_8\text{H}_8\text{O}_3\text{N}$ , in white needles, m. p.  $140^\circ$ . When treated in ethereal solution with magnesium pyrrole iodide, this ethyl ester yields  $\alpha$ -dipyrroylethane, m. p.  $236^\circ$  (cf. Oddo and Dainotti, A., 1912, i, 721), and the latter, when boiled with ammonium acetate in acetic acid, gives a blue-black powder which has the general properties of the pyrrole-blacks and the composition  $\text{C}_{12}\text{H}_8\text{O}_3\text{N}_3$ . T. H. P.

**Derivatives of Thiosemicarbazides and of Hydrazodithiocarbonamides.** E. FROMM [with E. LAYER and K. NERZ] (*Annalen*, 1923, 433, 1—17).—3 : 5-Diamino-4 : 1 : 2-thiodiazole,  $\begin{array}{c} \text{N} \cdot \text{C}(\text{NH}_2) \\ | \\ \text{N} \cdot \text{C}(\text{NH}_2) \end{array} > \text{S}$ , has already been obtained (Fromm, Briegleb, and Föhrenbach, A., 1922, i, 377; Busch, Schmidt, and others, A., 1913, i, 907; 1915, i, 317; Freund, Imgart, and Wischewiansky, A., 1894, i, 97; 1895, i, 400) by the action of concentrated hydrochloric acid on hydrazodithiocarbonamide. A better yield is obtained by oxidising the latter by means of warm, aqueous hydrogen peroxide; the dithienol form of the diamide becomes oxidised to a cyclic disulphide, which undergoes hydrolytic fission, with loss of sulphur, water being then eliminated from the resulting hydroxy-thienol derivative. The presence of two amino-groups in the product is demonstrated by the formation of a benzylidene derivative, pale yellow crystals, m. p.  $218^\circ$ , and of dibenzoyl and diacetyl derivatives, white; microcrystalline powders, of m. p. above  $280^\circ$ . The latter is also formed, together with phenylthiocarbimide, by the action of boiling acetic anhydride on  $\alpha$ -phenyl- $\beta$ (3 : 5-diamino-4 : 1 : 2-thiodiazolyl)-carbamide, m. p. above  $280^\circ$  (darkens at  $210^\circ$ ), which is produced by the action of phenylthiocarbimide on the thiodiamine in boiling, aqueous-alcoholic solution. The action of cyanogen on a warm 50% aqueous-alcoholic solution of the thiodiamine gives a compound, small, reddish-brown crystals, m. p. above  $280^\circ$  (blackens at  $200^\circ$ ), which has, perhaps, the formula,  $\text{CN} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{N} \\ | \quad | \\ \text{S} - \text{C} \cdot \text{NH}_2 \end{array}$ , since it gives a dibenzylidene derivative, a black or brownish-black, amorphous powder.

Hydrazodithiocarbonamide is converted by the action of boiling 10% hydrazine hydrate solution into 4-amino-1-thiol-2 : 3 : 5 : 6-tetrazine (or 3 : 4-diamino-5-thiol-1 : 2 : 4-triazole), yellow

needles, m. p. 217°, which gives the following derivatives: *benzyl*, white leaves, m. p. 220°, *benzoylbenzyl*, a microcrystalline powder, m. p. 198°, *acetylbenzyl*, an amorphous powder, m. p. 198—200°, *acetyl*, a white powder, m. p. 265°, *benzylidene*,  $+2\text{H}_2\text{O}$ , m. p. 270°. The latter is oxidised by means of hydrogen peroxide to a *disulphide*, a yellow powder, m. p. 265°; with lead acetate, it gives a lead salt.

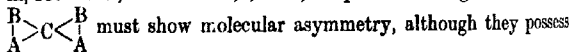
Diphenylhydrazodithiocarbonamide is converted by the action of boiling 10% hydrazine hydrate solution, or of warm dilute sodium hydroxide solution, into 3-anilino-5-thiol-4-phenyl-1:2:4-triazole (Busch and Ulmer, A., 1902, i, 575), which gives a *benzoyl* derivative, m. p. 187°, and a *benzyl* derivative, m. p. 154°, and is converted by the action of cold 50% sulphuric acid, warm aqueous-alcoholic hydrogen peroxide, or faintly acid ferric chloride solution, into a *disulphide*, a yellow, amorphous powder (*diacetate*,  $+ \text{H}_2\text{O}$ ), lemon-yellow crystals, m. p. 214°. The latter is converted by means of warm alcoholic sodium hydroxide solution into 3-anilino-4-phenyl-1:2:4-triazole (Busch and Bauer, A., 1900, i, 414).

Diphenylhydrazodithiocarbonamide is converted, in boiling alcoholic solution, by means of phenylhydrazine, iodine, or ferric chloride and hydrochloric acid, or, in cold, dilute sodium hydroxide solution, by means of hydrogen peroxide, into 3:5-dianilino-4:1:2-thiodiazole (*dibenzoyl* derivative, m. p. 198—199°) (Freund and Wischewiansky, A., 1894, i, 907; Busch and Schmidt, A., 1913, i, 907). The use of ferric chloride leads also to the formation of 3:5-dithio-4-phenyl-1:2:4-triazole, lemon-yellow needles, m. p. 230°, *dibenzyl* derivative, pale yellow crystals, m. p. 114°.

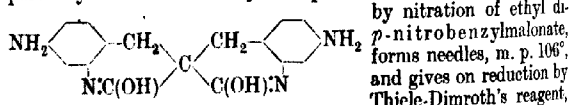
The action of hydrogen chloride, in boiling glacial acetic acid solution, on diphenylhydrazodithiocarbonamide, gives 3-anilino-5-thiol-4:1:2-thiodiazole (Busch and Schmidt, *loc. cit.*; Freund and Imgart, A., 1895, i, 400), which forms a *benzyl* derivative, white needles, m. p. 144°; it is oxidised by means of hydrogen peroxide in warm aqueous alcoholic solution to a *disulphide*, an orange-coloured precipitate, m. p. 227°, which is converted by the action of boiling, alcoholic sodium hydroxide solution into 3-anilino-4:1:2-thiodiazole, m. p. 170°.

W. S. N.

**Spirans. X. Ethyl Di-*op*-dinitrobenzylmalonate and its Reduction Products. Synthesis of an Optically Active Spiran without an Asymmetric Carbon Atom.** DAN RADULESCU (*Bul. Șoc. Științe Cluj*, 1922, 1, 306—310; from *Chem. Zentr.*, 1923, iii, 139—140; cf. this vol., i, 1211).—Spirans of the general formula



no single asymmetric carbon atom. Such a spiran has been prepared by the author. *Ethyl bis-*op*-dinitrobenzylmalonate*, obtained



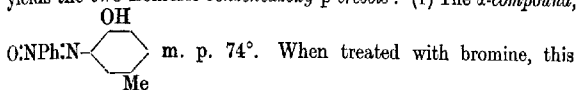
*bis-aminodihydrocurbostyrylspiran* (annexed formula). It is an

amorphous, white substance. The *dihydrochloride* forms flakes. The optically active *base* is obtained by means of silver bromo-camphorsulphonate. It has  $[\alpha]_D^{25} -84^\circ$  and is chemically identical with the racemic base.

G. W. R.

**Ortho-hydroxyazoxy-compounds.** DINO BIGIARI and RAOUL POGGI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 168—171).—Two isomeric azoxy-compounds containing a hydroxyl group in the ortho-position to the azo-group are formed as secondary products in the action of alkali and light on nitrosobenzene (Bamberger, A., 1900, i, 531; 1902, i, 505), but the yields are so small that their structures have not been determined.

Oxidation of benzeneazo-*p*-cresol by means of peracetic acid yields the two isomeric benzeneazoxy-*p*-cresols: (1) The  $\alpha$ -compound,



yields a *polybromo*-compound, m. p. 164—165°, from which, by reduction, the only base obtained is aniline. (2) The  $\beta$ -isomeride,  $\text{NPh:NO}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$ , m. p. 125°, which is converted by the action of bromine into a *dibromo*-derivative, m. p. 167°; reduction of the latter yields *p*-bromoaniline.

Certain reactions of the para-hydroxyazoxy-derivatives may be extended to the ortho-compounds. The first products of bromination of the  $\alpha$ - and  $\beta$ -benzeneazoxy-*p*-cresols are respectively  $\alpha$ -benzeneazoxy-3-bromo-*p*-cresol, m. p. 143°, and  $\beta$ -benzeneazoxy-3-bromo-*p*-cresol, m. p. 117°, each of these giving aniline and 6-amino-2-bromo-*p*-cresol when reduced by means of tin and hydrochloric acid.

In alkaline solution, permanganate oxidises azoxyphenols to isodiazocompounds with diverse velocities, the  $\beta$ -form of *p*-hydroxy-azoxybenzene exhibiting far greater resistance than the  $\alpha$ -isomeride (A., 1921, i, 364). Similarly, the oxidation of  $\beta$ -benzeneazoxy-*p*-cresol proceeds to so slight an extent that the normal diazo-compound obtained by acidifying the alkaline solution of the isodiazocompound gives but a feeble red coloration with  $\beta$ -naphthol; contrary to Bamberger's suggestion (A., 1900, i, 531), this reaction cannot be regarded as a means of characterising azoxyphenols. Owing to their different oxidisabilities, the two *o*-hydroxyazoxy-benzenes are to be considered as isomeric and not, as Bamberger at first supposed, as stereoisomeric; the compound, m. p. 78°, will have the  $\alpha$ -structure,  $\text{O:NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , and the isomeride, m. p. 108°, the  $\beta$ -structure  $\text{NPh:NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ .

It has been shown previously (A., 1922, i, 878) that nitrous acid acts on the grouping  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N(C)}\cdot$ , giving rise to a nitro-derivative with the nitro-group in the ortho-position to the hydroxyl, whilst it is without action on the grouping  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot$ . In agreement with this,  $\beta$ -benzeneazoxy-*p*-cresol remains unchanged when treated with nitrous acid, whereas the  $\alpha$ -isomeride yields  $\alpha$ -benzeneazoxy-3-nitro-*p*-cresol, m. p. 122°; further, benzeneazo-

cresol, by virtue of its  $\text{N}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$  group, yields a nitro-derivative with the nitro-group in the ortho-position to the hydroxyl.

Normal diazo-compounds, such as  $\text{NPh}\cdot\text{NH}$ , which are analogous to nitrous acid,  $\text{NH}\cdot\text{O}$ , resemble the latter in reacting with group-

ings containing a tervalent nitrogen atom and a hydroxyl group,  $\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . Thus, benzeneazo-*p*-cresol readily yields the compound  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}(\text{OH})\cdot\text{N}\cdot\text{NPh}$ , m. p.  $180^\circ$  (cf. Puxeddu and Maccioni, A., 1907, i, 798), and  $\alpha$ -benzeneazoxy-*p*-cresol the compound  $\text{O}\cdot\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}(\text{OH})\cdot\text{N}\cdot\text{NPh}$ , m. p.  $143^\circ$ .

Although it seems more justifiable to consider the difference between the two *o*-azoxy-compounds to be determined by the position of the oxygen atom in the azo-group, support is furnished to Baudisch's view (A., 1907, i, 356) by the observation that  $\beta$ -*o*-hydroxyazoxybenzene and  $\beta$ -benzeneazoxy-*p*-cresol react with difficulty with benzoyl chloride, acetic anhydride, or ethyl iodide, giving dense, oily products, whereas the corresponding  $\alpha$ -compounds readily yield crystalline products with these reagents. T. H. P.

**Condensation of Aryldiazonium Salts with Mono-alkylated Malonic Acids.** THOMAS KENNEDY WALKER (T., 1923, 123, 2775—2779).

**Ring Closure and Intensity of Colour.** JULIUS VON BRAUN and JON SEEMAN (*Ber.*, 1923, 56, [B], 2161—2164).—The intensity of the colour reactions given by certain dialkylanilines has been compared with those shown by allied compounds in which the nitrogen atom is present in a ring. The substances investigated include hydrols,  $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{R}$ , azo-compounds of the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NR}$ , and nitroso-compounds,  $\text{R}\cdot\text{NO}$ . In general, it appears that the absorption of light is much more marked with cyclic amines than with substituted anilines and that the length of the chain which is closed to a ring is unimportant; the phenomena do not appear to be explicable at the present time.

The following new compounds have been prepared incidentally: *Bis*-1-methyl-1:2:3:4-tetrahydroquinolymethane (from kairoline and formaldehyde in acid solution), a colourless, viscous liquid, b. p.  $235\text{--}240^\circ/1$  mm.; *bis*-N-methyl- $\alpha$ -methylidihydroindylmethane,  $\text{C}_{21}\text{H}_{28}\text{N}_2$ , a viscous liquid, b. p.  $235\text{--}240^\circ/1$  mm.; *p*-nitrobenzene-azo-*o*-anisidine, a brownish-red, microcrystalline powder, m. p.  $119\text{--}121^\circ$ ; *p*-nitrobenzeneazo-1-methyl-1:2:3:4-tetrahydro-6-quinoline, a microcrystalline, brown powder, m. p.  $147^\circ$ ; *p*-nitrobenzeneazo-N-methyl- $\alpha$ -methylidihydroindole, small, dark brown crystals, m. p.  $121^\circ$ ; *p*-nitrobenzeneazo-N-methylphenmorpholine, an almost black, crystalline powder, m. p.  $213^\circ$ . H. W.

**The Cyanine Dyes. VII. A New Method of Formation of the Carbocyanines. The Constitution of the Thioisocyanines and of Kryptocyanine.** WILLIAM HOBSON MILLS and WALTER THEODORE KARL BRAUNHOLTZ (T., 1923, 123, 2804—2813).

**Protein Studies. Crystalline Egg-albumin Salts which are Precipitated by Salts Other than Ammonium Sulphate.** S. P. L. SØRENSEN and S. PALITZSCH (*Z. physiol. Chem.*, 1923, 130, 72—83).—Egg-albumin may be obtained in a crystalline condition by the addition of a mixture of primary and secondary ammonium phosphate. The product resembles in crystalline form that obtained by the use of ammonium sulphate. The values of factor  $r$  = (weight of protein [containing water of crystallisation] / weight of protein nitrogen), for different preparations were determined. For protein precipitated at  $p_H$  4.81,  $r$  = 7.89, and at a  $p_H$  5.48,  $r$  = 8.12. For protein precipitated by ammonium sulphate,  $r$  = 7.86. The figures do not decide conclusively whether a different salt is precipitated in the two cases. The solubility of the protein in presence of ammonium sulphate increases rapidly with increase of  $p_H$ , i.e., at constant ammonium concentration, the solubility decreases with increase of phosphoric acid.

W. O. K.

**Hydroxypyrrroles in Proteins.** N. TROENSEGAARD (*Z. physiol. Chem.*, 1923, 130, 84—86; cf. this vol., i, 615).—Protein (gliadin) was acetylated (acetyl value, 36.3) and then methylated (methoxyl value, 20.5). The product was reduced with sodium in amyl-alcoholic solution and fractionated. The ether-soluble pyrrole fraction contained the greatest amount of methoxyl. Only about one-third of the total methoxyl survived the reduction. It would appear that there is more hydroxypyrrrole in gliadin than is detected by the usual analysis.

W. O. K.

**The Amino-acids of Zein.** H. D. DAKIN (*Z. physiol. Chem.*, 1923, 130, 159—168).—With the help of the butyl alcohol method (A., 1921, i, 66) an analysis has been made of zein, and the following constituents have been found: alanine, 3.8%; leucine, 25%; phenylalanine, 7.6%; tyrosine, 5.2%; proline, 8.9%; aspartic acid, 1.8%; glutamic acid, 31.3%;  $\beta$ -hydroxyglutamic acid, 2.5%.

W. O. K.

**Peroxydase. IV. The Peroxydase Activity of Oxyhæmoglobin.** RICHARD WILLSTÄTTER and ADOLF POLLINGER (*Z. physiol. Chem.*, 1923, 130, 281—301).—Systematic investigation has been made of the peroxydase activity of crystalline oxyhæmoglobin, by weighing the amount of purpurogallin produced from pyrogallol in presence of hydrogen peroxide under definite conditions. With a constant quantity of oxyhæmoglobin from horse-blood, the yield of purpurogallin increases with the amount of hydrogen peroxide, and so also with increasing oxyhæmoglobin and constant hydrogen peroxide. In neither case is the relation quite linear. The peroxydase activity does not alter with repeated recrystallisation, but differs from the activity of a simple solution of blood corpuscles, in which the peroxydase is hindered in its action by the catalase. A comparison of the activity of various types of hæmoglobin of various species of animals shows that that from horse-blood is the most active and that the others follow in the following order, dog, ox, and pig. The activity is approximately expressed

 $xx^*2$

by the formula  $a = ac^{1/n}$ , where  $1/n = 0.188, 0.229, 0.214$ , and  $0.215$ , for horse, dog, ox, and pig respectively, for constant hydrogen peroxide and varying hæmoglobin.

W. O. K.

**Natural Porphyrins. III. Exogenous Porphyrin Formation and Excretion.** HANS FISCHER and KARL SCHNELLER (*Z. physiol. Chem.*, 1923, 130, 302—325).—After the administration of blood, Kammerer's porphyrin has been found in the faeces in addition to the small amounts of coproporphyrin normally present. The adsorption spectra of these spectra has been investigated fully. Kammerer's porphyrin on treatment with ferrous acetate in acetic acid solution combines with iron and Kammerer's hæmin is formed. Exposure to bright sunlight of a person secreting Kammerer's porphyrin as a result of administration of blood gave negative results. Porphyrin is obtained from hæmin by the action of sodium amalgam in alkaline solution.

W. O. K.

**Analysis of Tuberculinic Acid.** ELMER E. BROWN and TREAT B. JOHNSON (*J. Biol. Chem.*, 1923, 57, 199—208).—On purification, tuberculinic acid (cf. this vol., i, 160, 965) loses guanine, leaving a stable trinucleotide containing adenine, thymine, and cytosine. The absence of uracil from the molecule has been confirmed.

E. S.

**The Decomposition Products of Gelatin.** WL. GULEWITCH (*Z. physiol. Chem.*, 1923, 130, 152—158).—From the product of the hydrolysis of gelatin by sulphuric acid an amino-acid has been isolated as the nitrate  $C_6H_{14}O_2N_4.HNO_3$ , m. p.  $222^\circ$ ,  $[\alpha]_D +0.16^\circ$ . The copper salt forms blue rosettes,  $(C_6H_{14}O_2N_4)_2.Cu(NO_3)_2$ , m. p.  $227^\circ$  (decomp.). The acid is apparently racemic arginine, obtained previously by Kutscher (*Z. physiol. Chem.*, 1898, 26, 114) by the tryptic decomposition of fibrin. It is considered probable that the racemic form arises by racemisation of *d*-arginine by the acid used in the hydrolysis.

W. O. K.

**The Combination of Deaminised Gelatin with Hydrochloric Acid.** DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, 6, 95—104).—When prepared without heat, deaminised gelatin, the isoelectric point of which is at  $P_H 4.0$ , contains 0.0004 equivalent of nitrogen per g. less than the original protein, an amount which is equivalent to the amino-nitrogen present in gelatin as indicated by Van Slyke's method. The difference (0.00045 equivalent) between the maximum combining capacities of gelatin and of deaminised gelatin for hydrochloric acid is practically equivalent to the loss in amino-nitrogen during the deaminising process. This is additional evidence that the combination between protein and acid is a chemical combination. The combining capacity of gelatin for hydrochloric acid (cf. A., 1922, i, 882) has been corrected to 0.00089 mols. per g. of protein.

E. S.

**Action of Chymosin and Pepsin. IX. The Different Behaviour of the Stomach Enzymes of the Calf and Pig with Acid on Heating.** OLOF HAMMARSTEN (*Z. physiol. Chem.*, 1923, 130, 55—71).—Evidence is brought to show that there is in the stomach of the pig only one enzyme. This is a pepsin and both

coagulates milk and hydrolyses protein. In the stomach of the calf there exist two enzymes, pepsin as before, and also chymosin which only coagulates milk. Whilst pepsin is the less resistant to alkali, as was previously shown (A., 1922, i, 958), it is now demonstrated that chymosin is the less resistant to acid. When heated in presence of 0.2% hydrochloric acid, the milk coagulating action of the extract of calf stomach decreases in the ratio 1 : 1.1, and the pepsin action only in the ratio 1 : 1.4. In the case of the extract of pig's stomach, the milk coagulating action decreases in the ratio 1 : 1.5, and the pepsin in the ratio 1 : 1.4. W. O. K.

**Stoicheiometrical Relationship between Invertase and Silver Nitrate.** H. VON EULER and K. MYRBÄCK (*Svensk Kem. Tidskr.*, 1922, 34, 222—231; from *Chem. Zentr.*, 1923, iii, 314; cf. A., 1922, i, 959).—From experiments on the inactivation of invertase by silver nitrate in solutions of varying hydrogen-ion concentration, it is concluded that a stoicheiometrical relationship exists between the enzyme and the silver nitrate which inactivates it. The silver equivalent is calculated as 5400. G. W. R.

**Molecular Condition and Stability of Saccharase.** H. VON EULER, K. JOSEPHSON, and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 130, 87—107).—It has been shown previously (this vol., i, 721) that highly purified saccharase can by diffusion be separated from material of high molecular weight associated with it. It is now found that the ratio of the rates of diffusion corresponds with a molecular weight of about 20,000 for the saccharase.

The activity of saccharase is decreased by alcohol, but reversibly, so that the activity returns again when the alcohol is removed. However, alcohol also causes an irreversible destruction of the saccharase. This destruction is a maximum with 60% alcohol and slowly decreases with more concentrated alcohol. The results agree qualitatively but not quantitatively with those of Hudson and Paine (A., 1910, i, 798). Apparently, this irreversible destruction depends to some extent on the degree of purity of the saccharase preparation. Some preparations of saccharase lose their activity on heating according to the law of unimolecular reaction, whereas other preparations of the same activity do not follow this law. Probably two enzymes exist, one of which possesses much greater thermostability than the other. However, the affinities for the substrate of the heated and the unheated enzyme solution are very similar. This would scarcely be expected if two enzymes were present and one was thermolabile. These results may be explained on the hypothesis that the stability of the enzyme is determined by other groups of the enzyme molecule than those which determine the affinity, and that the latter are the same in the two enzymes.

The rate of destruction of the dried enzyme is much less than that of the solution. W. O. K.

**The Relation of the Thermolability of Malt Diastase to Acidity.** EFR. ERNSTRÖM (*Biochem. Z.*, 1923, 144, 40—41).—At a  $p_H$  of 5.2, the resistance of malt diastase to inactivation, when

exposed for one hour to a temperature of 55°, is at a maximum (cf. Lüers and Lorinser, *Biochem. Z.*, 1922, **133**, 487). J. P.

**The Action of Arsenic and Antimony Compounds on the Fermentative Function of the Organism. I. The Action of certain Arsenic and Antimony Preparations on Ptyalin.** J. A. SMORODINCEV and FR. E. A. ILIIN (*Biochem. Z.*, 1923, **141**, 297—303).—Potassium and sodium arsenites and arsenates, antimony trichloride, and antimonyl potassium tartrate inhibit the action of ptyalin on starch, the antimony compounds being more active than those of arsenic. In great dilutions (0.00004%), antimony trichloride accelerates the action of the enzyme, a result which is ascribed, not to any specific action of the antimony, but to the hydrochloric acid formed from the salt. In higher concentrations, hydrochloric and tartaric acids inhibit ptyalin, the latter exerting much the more marked effect. J. P.

**Enzyme Action. XXIV. The Kinetics of the Ester-hydrolysing Actions of some Tissue and Tumor Extracts.** KANEMATSU SUGIURA, HELEN MILLER NOYES, and K. GEORGE FALK (*J. Biol. Chem.*, 1923, **56**, 903—920).—Measurements have been made of the reaction velocity of the hydrolysis of glyceryl triacetate by extracts of the Flexner-Jobling rat carcinoma under different conditions of concentration and acidity. The results are similar to those which have been obtained with other enzymes. E. S.

**Enzymic Hydrolysis of Hippuric Acid.** A. CLEMENTI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 172—174).—The experimental results described confirm (cf. Mutch, A., 1912, ii, 579) the presence in the animal organism of an enzyme, termed hippuricase, which hydrolyses hippuric acid to benzoic acid and glycine and occurs in the kidneys of mammals in general and in pig's liver. Although its amidolytic activity is analogous to that of erepsin or trypsin, hippuricase is biochemically distinct from these enzymes. T. H. P.

**Ferments. II. Lability of Soja Urease and the Question of Auxoureases and Coenzymes. III. Mechanism of the Action of Robinia Urease.** SATOSU NAKAGAWA (*Mitt. med. Fak. Kais. Univ. Tokyo*, 1922, **28**, 383—427; from *Chem. Zentr.*, 1923, iii, 395).—Soja urease is very labile in dilute solution and its effect at high temperatures is less than that calculated from the time and the amount of enzyme present. The auxourease described by Jacoby inhibits the decomposition of urease. This inhibition is not shown by sodium nucleate, or the ash constituents of the substances containing the auxourease. The co-enzyme effect of enzyme solutions inactivated by alkalis, acids, or by heating is explained as a protective action. Whether auxoureases exert an activating effect can only be decided with preparations free from proteins and their hydrolytic products. Phosphates and acetates have no protective effect on urease, neither do they influence the effect of auxoureases. It is confirmed that the diminished

activity of urease with increased volume of liquid holds also with constant concentration of urea.

*Robinia urease* has optimum  $p_H$  7.4. Phosphates have no effect between 0.02 and 0.04 *M*. Urea exerts an inhibitory effect in concentrations above 10%. It is less labile than soja urease.

G. W. R.

**Bacterial Tyrosinase.** C. STAPP (*Biochem. Z.*, 1923, **141**, 42—69).—A tyrosinase closely resembling that of fungi is present in cultures of the bacteria from the root nodules of *Soja hispida*, various species of *Lupinus*, *Coronilla varia*, *Genista tinctoria*, *Sarothamnus scoparius*, and *Tetragonolobus purpureus*. Soja tyrosinase is capable of oxidising the barium salt of tyrosinesulphonic acid, hydroxyphenylethylamine hydrochloride, and to a less extent  $\beta$ -resorcylic acid. Gentisic acid, 2:4- and 2:5-dinitrobenzoic acids, anthranilic acid, phenylglycine and  $\beta$ -phenylpropionic acid are not oxidised. Bacterial tyrosinase acts more quickly in cultures killed by chloroform than in the presence of the living bacteria. It is regarded as an endocellular enzyme, and does not pass through a porcelain filter. The various tyrosinases investigated were all inactivated at temperatures between 60° and 65°, but they may be reactivated by shaking with oxygen even after subjection to temperatures of 75°. With increasing temperature, the rate of oxidation by bacterial tyrosinase rises, the optimum appearing to be close to the inactivation temperature. The range of action lies between  $p_H$  5 and  $p_H$  10.5, with an optimum at  $p_H$  8. By means of bacterial tyrosinase, the presence of tyrosine in 0.005% concentration may be demonstrated. The intermediate formation of homogentisic acid was not detected during the action of the enzyme on tyrosine.

J. P.

**Extraction of Vitamins from Yeast and Rice Polishings with Various Water-miscible Solvents.** CASIMIR FUNK, BENJAMIN HARROW, and JULIA B. PATON (*J. Biol. Chem.*, 1923, **57**, 153—162).—When judged by the inactivity of the residues, the best solvents appear to be 70% alcohol in the case of yeast and 60% alcohol in the case of rice polishings. Very active extracts may also be obtained with acetone; moreover, such extracts contain a comparatively small proportion of nitrogenous impurities. The amounts of vitamins-B and -D extracted by different solvents appear to run parallel; no relation appears to exist, however, between these vitamins and the coferment. Extracts of rice polishings have a greater activity on rats than on pigeons. E. S.

**Glucokinin. II.** J. B. COLLIP (*J. Biol. Chem.*, 1923, **57**, 65—78).—Methods are described for the preparation of extracts of glucokinin (this vol., i, 967) from various plants. Injections of such extracts into normal rabbits produce a marked hypoglycæmia, which, however, may not become evident for some days or even weeks, followed by death. When the blood-serum obtained from such animals immediately prior to, or just after, death is injected into a second rabbit, similar results are produced. •A depancreatised

dog has been maintained alive for sixty-six days, only three injections of glucokin (onion extract) being made during this period.  
E. S.

**Organic Derivatives of Silicon. XXIX. Preparation, Properties, and Condensation Products of Di-*p*-tolylsilicane-diol.** HERBERT SHEPPARD PINK and FREDERICK STANLEY KIPPING (T., 1923, 123, 2830—2837).

**The Preparation and Properties of some Phenylstannanes,  $\text{Sn}_n\text{Ph}_{2n+2}$ , and the Application of Microchemical Methods to the Determination of their Constants. Tervalent Tin.** J. BÜSEKEN and J. J. RUTGERS (*Rec. trav. chim.*, 1923, 42, 1017—1025).—Magnesium phenyl bromide reacts with stannic chloride to give tin diphenyl, tetraphenylmonostannane, hexaphenyldistannane, dodecaphenylpentastannane, and tin, together with some tin tetraphenyl. The analyses of these compounds were carried out by microchemical means, and their densities determined by flotation. It was found that hexaphenyldistannane in dilute benzene solution has only half the normal molecular weight, and that it will combine with iodine to form triphenylmonostannane iodide. It is therefore considered that tin in this compound is trivalent. Dodecaphenylpentastannane is regarded as having the formula  $\text{Sn}(\text{SnPh}_2)_4$ .  
H. H.

**Organic Mercury Mercaptides.** GEORG SACHS [with HERBERT ANTOINE, and, in part, LEO SCHLESINGER] (*Annalen*, 1923, 433, 154—163).—A series of compounds of the type  $\text{R}^1\text{-Hg-S-R}^2$  has been prepared by the interaction of alkyl- or aryl-mercuric halides and sodium mercaptides, in anhydrous alcoholic or acetone solution. The compounds are white and crystalline, easily soluble in most organic solvents, and volatile in steam. They are somewhat readily hydrolysed by means of dilute acids, giving mercaptans. The lower members of the series possess an unpleasant odour.

*Ethylmercuric ethylmercaptide* has m. p. 0—3°. *Ethylmercuric phenylmercaptide* has m. p. 61°. *Phenylmercuric ethylmercaptide* forms white, glistening needles, m. p. 56°. *Phenylmercuric phenylmercaptide*, clusters of prismatic needles, has m. p. 105—106°. *Phenylmercuric benzylmercaptide* has m. p. 96°. *Benzylmercuric phenylmercaptide* has m. p. 96°. Phenylmercuric ethylmercaptide reacts with ethyl iodide in boiling absolute alcoholic solution to give a double compound,  $\text{Ph-Hg-SEt,SEt-HgI}$ , m. p. 140°, whereas in 96% alcoholic solution, phenylmercuric iodide is formed. If benzyl iodide is used, in anhydrous alcoholic solution, the products are phenylmercuric iodide and benzyl ethyl sulphide. The latter forms the following *additive* compounds by the action of alcoholic mercuric chloride:  $\text{EtS-C}_6\text{H}_5\cdot\text{HgCl}_2$ , m. p. 83°, and  $\text{EtS-C}_6\text{H}_5\cdot 2\text{HgCl}_2$ , m. p. 142°.  
W. S. N.

## Physiological Chemistry.

**The Significance of the Dual Function of Hæmoglobin in relation to the Mechanism of the Chemical Regulation of Respiration.** ROBERT GESELL (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, 63, 393—394).—In certain conditions there may be a broken co-ordination of the dual function of hæmoglobin (namely, as a carrier of oxygen, and as a source of alkali to the plasma), with abnormal breathing resulting. Response of the respiratory centre to changes in acidity is discussed, as well as the effect of the administration of carbon dioxide on conditions arising from a lack or excess of oxygen. CHEMICAL ABSTRACTS.

**Gas and Electrolyte Equilibria in the Blood. V. Factors Controlling the Electrolyte and Water Distribution in the Blood.** DONALD D. VAN SLYKE, HSIEN WU, and FRANKLIN C. McLEAN (*J. Biol. Chem.*, 1923, 56, 765—849).—This paper deals from a physico-chemical point of view with the distribution of electrolytes and water between corpuscles and serum and with the effect of various factors on this distribution. Assuming the applicability to blood of (1) the laws governing the distribution of a base between strong and weak acids, (2) Donnan's law of membrane equilibria, and (3) the laws of osmotic pressure, and making certain simplifying assumptions, expressions have been deduced which indicate the electrolyte and water distribution in blood and the changes which are produced in it by changes in  $P_H$ . Measurements of the changes actually produced by variations in the carbon dioxide tension have yielded results in approximate agreement with these expressions. The changes which occur are illustrated in the case of oxygenated blood. Thus, an increased acidity due to an increase in the carbon dioxide tension produces the following changes which are regarded as taking place simultaneously: (1) the transference of base from hæmoglobin to carbonic acid, (2) the migration of  $\text{Cl}^-$  ions from serum to cells and of  $\text{HCO}_3^-$  ions in the reverse direction to restore the membrane equilibria, and (3) the migration of water from serum to cells to restore osmotic equilibrium. For the mathematical treatment of the subject and certain deductions therefrom, the original must be consulted.

E. S.

**Carbon Dioxide Absorption Curve of Human Blood. III. A Further Discussion of the Form of the Absorption Curve Plotted Logarithmically, with a Convenient Type of Interpolation Chart.** JOHN P. PETERS (*J. Biol. Chem.*, 1923, 56, 745—750).—Absorption curves obtained by plotting  $\log(p_{\text{CO}_2})$  against  $\log(\text{CO}_2 \text{ vol.}\%)$  are more nearly straight lines than are those given by the  $P_H$ — $\text{MHCO}_3$  relation (cf. Peters and Eisenman, *ibid.*, 55, 709). Hence the former method is superior for the extrapolation or interpolation of points on an absorption curve. Further,

by plotting the carbon dioxide tension against the carbon dioxide content on logarithmic paper, and assuming a constant  $P_x$  value, a chart is obtained in which the  $P_H$  values are represented by parallel lines making an angle of  $45^\circ$  with the abscissa. Such charts can only be constructed for plasma, since  $P_x$  is not constant for whole blood.

E. S.

**The Oxygen Content of Capillary Blood.** F. VERZÁR and F. KELLER (*Biochem. Z.*, 1923, 141, 21—27).—Capillary blood collected from the ball of the finger shows an oxygen content similar to that of arterial blood. The average figure observed in normal individuals was 91% of saturation, falling in a few cases to 85%, but never below 82%. In uncompensated lung affections involving a diminution of respiratory surface values appreciably below normal were obtained. Muscular work in the normal person did not alter the oxygen content of capillary blood.

J. P.

**The Ammonia Content of the Blood.** V. HENRIQUES (*Z. physiol. Chem.*, 1923, 130, 39—44).—Estimations show that there is no appreciable difference between the ammonia content of the blood of the renal vein and that of the carotid artery or of the vena cava. This result does not confirm that of Nash and Benedict (*A.*, 1922, i, 191), who found increased ammonia in the renal vein, and suggested on this ground that ammonia is formed in the kidneys.

W. O. K.

**The Fatty Acids of Blood Plasma.** W. R. BLOOR (*J. Biol. Chem.*, 1923, 56, 711—724).—Results are given of a large number of analyses of the fatty acid and cholesterol (unsaponifiable matter) content of the blood plasma of fasting animals (pig, ox, sheep, dog). Considerable variations were observed between both the different species and the individuals of the same species. In all species, however, the ratios unsaponifiable matter : fatty acid and liquid fatty acid : total (solid + liquid) fatty acid appeared to be approximately constant, the values being roughly one half and two-thirds, respectively. The liquid fatty acid fractions gave high and relatively constant iodine numbers (110—160), indicating the presence of highly unsaturated acids. These results, together with the constancy in the melting points of the various fatty acid fractions, indicate that the compounds from which the fatty acids are derived have, in the plasma of fasting animals, a constant composition as regards saturated and unsaturated acids, and exist in definitely balanced relation to each other.

E. S.

**The Amino-acid Nitrogen of the Blood.** I. The Total Free Amino-acid Nitrogen in Blood. II. The Diamino-nitrogen in the Protein-free Blood Filtrate. III. The Occurrence of Peptide Nitrogen in the Blood. NATHAN F. BLAU (*J. Biol. Chem.*, 1923, 56, 861—866, 867—871, 873—879).—I. Estimations have been made of the amino-nitrogen content of a number of pathological bloods. II. Diamino-nitrogen has been estimated in the protein-free filtrates from pathological bloods. The values obtained, which range from 0.13 to 4.54 mg. per 100 c.c.

of blood, represent the difference in the amino-nitrogen content before and after precipitation of the basic amino-acids with phosphotungstic acid. III. No appreciable amount of peptide nitrogen is present in normal blood. Varying quantities, however, have been found in pathological bloods, but in insufficient amount to account for the undetermined nitrogen.

E. S.

**Amino-acids of the Blood. III. Influence of Toxic Anæmia and Blood-letting.** S. MARINO (*Arch. Farm. speriment. Sci. aff.*, 1923, 36, 88—96; cf. this vol., i, 1036).—The amino-acid content of the blood of the dog (1) is increased or diminished by repeated blood-letting, according as the repetitions occur at short or long intervals, and (2) under the action of hæmolytic poisons, diminishes during the period of the granules and Heinz bodies, and increases during the regeneration of the blood. In case (1) also the increase is related to the regeneration of the blood.

T. H. P.

**The Inter-relationship of Blood-fat and Blood-sugar.**

F. H. OLIVER and A. HAWORTH (*Lancet*, 1923, II, 114—116).—Evidence is adduced to show that the blood-sugar has a relation to the blood-fat other than that of a mere oxidising agent. Fat properly absorbed into the tissues appears to increase the storage of carbohydrate; if it is not so absorbed, or if it is mobilised by calcium, interference with the storage takes place. Practically all conditions which lead to a hyperglycæmia lead also to a lipæmia, probably owing to diminished oxidation. Injection of adrenaline causes a rise in blood-fat in addition to hyperglycæmia. In this case, since it is difficult to understand why the liberation of a large amount of oxidising material should be accompanied by an increase of the substance to be oxidised, it is suggested that both were stored and liberated together.

A. A. E.

**Blood Catalase.** W. VON MORACZEWSKI (*Biochem. Z.*, 1923, 41, 471—475).—Blood catalase is diminished in fevers and in shock conditions, and rises after ingestion of proteins and sugar and in diabetes. Phloridzin increases blood catalase although it diminishes the blood-sugar, whilst pilocarpine diminishes both. The enzyme is increased by adrenaline. In certain affections of cardiac and respiratory functions, strychnine lessens the catalase, whilst caffeine increases it. In general a diminution of red blood-corpuscles is associated with an increased catalase activity. J. P.

**The Action of Thyroxin. III. The Destruction of the Specific Action of Thyroxin by Blood in Vivo and in Vitro.** ENNO ROMEIS (*Biochem. Z.*, 1923, 141, 500—522).—The blood, serum, bile, and urine of dogs which have been given an intravascular injection of thyroxin in weakly alkaline saline have no effect, even when removed a few minutes after the injection, on the rate of development of tadpoles. The conclusion is drawn that thyroxin is rapidly changed and inactivated in the blood-stream. The activity of a thyroxin solution is lowered by retention for several hours in the body-cavity. By repeated intravenous injection of

thyroxin, the rate of destruction in the blood is lessened. For undiluted blood lowers the activity of thyroxin in vitro and after one to two hours' contact the blood-thyroxin solution becomes toxic to tadpoles. Serum alone and washed erythrocytes inhibit thyroxin, the latter being more active in this respect than the former. It is concluded that a mechanism exists in the blood for the regulation of the amount of thyroxin in response to the tissue requirements.

J. P.

**Chemical Changes in the Blood under the Influence of Drugs. II. Morphine.** H. V. ATRINSON and H. N. ETS. *Lab. Clin. Med.*, 1922, 8, 170—175).—Morphine increases the carbon dioxide combining power, and decreases the oxygen combining power of the blood. The content of sugar, creatinine, a total fat is increased, and that of lecithin and cholesterol decreased.

CHEMICAL ABSTRACTS.

**The Effect of Buffer Salts on Blood Coagulation.** BENJAMIN JABLON (J. Lab. Clin. Med., 1923, 8, 679—681).—Dipotassium hydrogen phosphate or potassium dihydrogen phosphate causes a striking inhibition of blood coagulation, similar to that produced by sodium citrate. The blood remained incoagulable for forty-eight hours; with the former phosphate, it was bright red, and with the latter, very dark red. The latter salt also increased the viscosity of the blood; hæmolysis was fairly marked, but only slight in the former case.

CHEMICAL ABSTRACTS.

**Adsorption of Protein Degradation Products by the Blood corpuscles in Vivo and in Vitro. II. Adsorption by the Red Blood-corpuscles.** B. SBARSKY (*Biochem. Z.*, 1923, 141, 33—36).—It is shown that the adsorption of protein degradation products by blood-corpuscles (this vol., i, 411) is a property of the erythrocytes both in vivo and in vitro. The adsorption does not proceed according to the Freundlich equation.

J. P.

**Adsorption of Protein Degradation Products by the Blood corpuscles in Vivo and in Vitro. III. The Adsorption Capacity of the Blood of various Animals.** B. SBARSKY and D. MICHLIN (*Biochem. Z.*, 1923, 141, 37—39).—A varying capacity to adsorb foreign proteolytic products (diphtheria-toxin) in the blood is shown by different animals. This increases in the order given: rat < dog < horse < guinea-pig < hen < pigeon. A parallel is drawn between this order and the susceptibility of the animal to the action of the toxin.

J. P.

**Viscosity of Blood-serum and its Relation to the Content of Albumin and Globulin.** S. M. NEUSCHLOSZ and R. A. TRELLIS (*Anal. Asoc. Quím. Argentina*, 1923, 11, 73—77).—Whilst the viscosity of human blood-serum may be correlated with its protein content the data given by the authors for forty sera show that there is no evidence for a correlation with the albumin-globulin ratio.

G. W. R.

**Study of the Condition of Several Inorganic Constituents of Serum by Means of Ultrafiltration.** B. S. NEUHAUSEN and J. B. PINCUS (*J. Biol. Chem.*, 1923, **57**, 99—106).—Analyses of ultrafiltrates of pig's serum indicate that chlorides, phosphates, sodium, and potassium are present entirely in a diffusible form, whilst 30—50% of the calcium is non-diffusible (cf. Cushny, A., 1920, i, 508).

E. S.

**Relative Precipitating Capacity of certain Salts when Applied to Blood Serum or Plasma and the Influence of the Kation in the Precipitation of Proteins.** PAUL E. HOWE (*J. Biol. Chem.*, 1923, **57**, 241—254).—The relative precipitating capacities of a number of salts have been compared, using as criterion of efficiency the increases in concentration which are necessary to precipitate the successive protein fractions. The results are presented in detail in the original, and agree, in general, with those obtained by others. For each particular salt, the increase in concentration required to precipitate succeeding protein fractions is constant, although not necessarily the same for different salts.

E. S.

**Changes in the Proteins and the Gelafication of Formalised Blood-serum.** R. R. HENLEY (*J. Biol. Chem.*, 1923, **57**, 139—151).—Addition of formaldehyde to serum causes the various protein fractions to become progressively less soluble in ammonium sulphate. With high concentrations of formaldehyde, the albumin and  $\psi$ -globulin fractions disappear; with low concentrations, an equilibrium is reached. The rate of transformation is, for a given serum, proportional to the concentration of formaldehyde, as also is the rate of gelafication of the serum. With a constant concentration of formaldehyde, the rate of gelafication is proportional to the concentrations of protein and salts in the serum.

E. S.

**Antipepsin.** ERNST STOLZ (*Biochem. Z.*, 1923, **141**, 483—487).—The antipeptic action of blood-serum is ascribed, not to the presence of a specific antipepsin, but to the capacity of serum-albumin to adsorb pepsin and so lower its activity. The absence of the supposed anti-ferment from the alimentary mucous membrane cannot be regarded as a causal factor in gastric or duodenal ulcer.

J. P.

**The Nature of the Antitryptic Action of Serum and its Biological Significance.** A. A. EPSTEIN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 48—50).—The inhibition of tryptic digestion by serum is due slightly to globulin and largely (and proportionately) to the amount of albumin present. Trypsin was quantitatively recovered, after prolonged incubation with serum, by precipitation of the proteins with colloidal iron or ethyl alcohol. After digesting casein, no trypsin was recovered, but the latter was recovered from admixture with serum and casein when digestion did not take place. The action is of the nature of an interference phenomenon.

CHEMICAL ABSTRACTS.

**The Diastase Activating Property of Serum.** The rôle of the Pancreas in Carbohydrate Metabolism. TORAO KOGA (*Biochem. Z.*, 1923, 141, 410—429).—The activating properties of serum on diastases observed by Wohlgemuth (*Biochem. Z.*, 1911, 33, 303) have been further investigated. Pancreatic diastase is eight times as active in the presence of serum as it is in pure aqueous solution. An artificial salt solution of the same composition as the serum salts has only half of the activating effect of the serum. It is concluded that a diastase activating substance other than the salts is present in blood-serum. It is regarded as being colloidal in nature, since dialysed serum retains in large part its activity, whilst serum treated with colloidal iron loses most of its activating powers. Adsorption experiments with negatively and positively charged adsorbents on blood-serum show that the active principle has no specific electric charge, but may be to a small extent negatively charged. It is insoluble in ether and light petroleum and is stable to acids and alkalis. Putrefying serum is still active. Washed blood-corpuscles and neutralised urine show a similar activating effect. Dialysed urine loses but little of its activity. The activating substance is also present in milk. In starving dogs, the serum from the pancreatico-duodenal vein increases the action of diastase to a greater extent than that from systemic blood-serum, but this difference is not observed in dogs which have been fed. It is concluded that glycogenolysis in the liver is produced, not by a direct impulse, but indirectly through the pancreas, which is stimulated to produce a hormone (the diastase activating substance of the blood) which then passes to the liver.

J. P.

**Inorganic Metabolism. I. The Influence of Cod Liver Oil on Calcium and Phosphorus Metabolism. II. The Influence of Crude Fibre and of Protein on Calcium and Phosphorus Metabolism.** B. SJÖLLEMA (*J. Biol. Chem.*, 1923, 57, 255—270, 271—284).—I. Rabbits were used as experimental animals. Administration of cod liver oil produced an increased retention of calcium and phosphorus independently of whether the animals were in positive or negative calcium balance. In the former case, it was mainly the urinary, and in the latter, the faecal, calcium output which was diminished. The total output of phosphorus was independent of the amount of calcium in the food. The amount of calcium excreted in the faeces may exceed considerably that administered in the food.

II. Addition of indigestible material to the diet causes an increased excretion of calcium in the faeces and thus tends to produce a negative calcium balance. A high protein diet favours retention of calcium (cf. this vol., i, 511).

E. S.

**Intermediary Metabolism of Carbohydrates.** P. A. SHAFFER (*Physiol. Rev.*, 1923, 3, 394—437).—A comprehensive review with an extensive bibliography. According to the view now prevalent lactic acid represents the main intermediate in dextrose metabolism. There is no obstacle to the belief that glyceraldehyde,

dihydroxyacetone and methylglyoxal (together with the hexose phosphate, "lactacidogen") represent the main intermediates between glycogen or dextrose and lactic acid. The reaction dextrose  $\rightleftharpoons$  lactic acid is reversible, but the preponderating reaction in the presence of oxygen is lactic acid  $\rightarrow$  dextrose. It is difficult to believe that dextrose is oxidised by way of lactic and pyruvic acids and acetaldehyde. It is not unlikely that it is oxidised to a single molecule of ketolytic substance without previous splitting to triose.

CHEMICAL ABSTRACTS.

**Intermediary Protein Metabolism.** II. The rôle of the Liver in the Production of Urea. III. The rôle of the Liver in the Metabolism of Amino-acids. IV. The rôle of the Liver in the Intermediary Metabolism of Amino-acids. A. GOTTSCHALK and W. NONNENBRUCH (*Arch. exp. Path. Pharm.*, 1923, 99, 261—269, 270—299, 300—314).—II. Solutions of pure amino-acids and of mixtures of amino-acids were injected into the dorsal lymph sac of normal frogs, and of frogs from which the liver had been extirpated, and the resulting changes in the concentration of urea nitrogen and residual non-protein nitrogen in the blood were observed. It was found that removal of the liver made no difference to these changes, which consisted in a definite rise in the concentration of urea nitrogen following the administration of the amino-acids. A similar but less pronounced rise in urea concentration followed administration of casein. It was therefore concluded that urea formation is not a special function of the liver in the frog.

III. In the case of rabbits and dogs, a rise in both urea and non-urea fractions of the non-protein nitrogen of the blood was observed to follow intra-duodenal administration of amino-acids, and this rise is quantitatively the same in blood from all parts of the circulation, except where an increased autolysis of the liver cells brought about by the conditions of the experiment may cause an increase of nitrogenous products in the hepatic vein. The feeding of casein and the slow, continuous administration of amino-acids bring about little change in the nitrogen of the blood. It is concluded that the part played by the liver in the metabolism of the amino-acids which are absorbed into the blood-stream is not a predominant one, but that every cell in the body may share in his process to an extent which is determined by its individual needs at the moment.

IV. The fourth paper deals with the extension of these results to man.

C. R. H.

**Nuclein Metabolism.** I. Adenine Nucleotide in Human Blood. HENRY JACKSON, jun. (*J. Biol. Chem.*, 1923, 57, 121—128).—Adenine has been isolated from human blood in the form of its inorganic salt under conditions which indicate that it was originally present as adenine nucleotide. Normal whole blood appears to contain 15—25 mg. of adenine nucleotide per 100 c.c.; this accounts for a considerable portion of the undetermined nitrogen. E. S.

**To What Extent is Cetyl Alcohol Absorbable (by Animals)?** K. THOMAS and B. FLASCHENTRÄGER (*Skand. Arch. Physiol.*, 1923, 43, 1—5; from *Chem. Zentr.*, 1923, iii, 266).—Feeding experiments with dogs showed that cetyl alcohol is absorbed only to a very slight extent. As the m. p. of the alcohol is 49.5° and therefore above body temperature, experiments were carried out with *cetyl acetate*, m. p. 19°. This also was utilised to an insignificant extent and it is concluded to be of no value as a food material.

G. W. R.

**Nutritive Values of Starch and Sucrose.** GEORG VON WENDT (*Skand. Arch. Physiol.*, 1923, 43, 264—274; from *Chem. Zentr.*, 1923, iii, 266).—For fat production in cattle and pigs sucrose has only 75 to 80% of the value of starch. For maintenance, however, the two substances are equal, whilst for energy production sucrose is superior to starch by at least 10%. This is probably due to the fact that starch is absorbed as dextrose, whilst sucrose yields *lævulose* as well as dextrose. Fat synthesis from dextrose probably begins by way of acetaldehyde, whereby two carbon atoms are lost as carbon dioxide. The keto-group in *lævulose* is easily broken down. Two mols. of *lævulose* are necessary for the formation of aldol. Thus only two carbon atoms from *lævulose* as against four carbon atoms from dextrose are utilised for fat synthesis. *Lævulose* will also be less efficient than dextrose for glycogen synthesis. For the production of mechanical energy *lævulose* may be more efficient than dextrose.

G. W. R.

**Age and Chemical Development in Mammals.** C. R. MOULTON (*J. Biol. Chem.*, 1923, 57, 79—97).—A large amount of data on the composition of animals at various stages of development has been collected. When this is recalculated on a fat-free basis, it is found that the relative water content of mammals decreases, and the relative protein and ash content increases, from earliest life until chemical maturity is reached, following which a fairly constant composition is shown. The ratio, age at which chemical maturity is reached/total life cycle, is fairly constant for mammals. The relative water content of mammals at birth is smaller the greater the maturity.

E. S.

**Influence of the Positive Nitrogen Balance on Creatinuria during Growth.** VICTOR JOHN HARDING and OLIVER HENRY GAEBLER (*J. Biol. Chem.*, 1923, 57, 25—45).—The total creatine production in growing dogs increases with the protein content of the diet until a maximum, which corresponds with the maximum positive nitrogen balance, is reached. With a constant nitrogen intake, the creatine excretion varies inversely as the nitrogen gain. The total creatine coefficient (cf. this vol., i, 169) of puppies is more than twice the creatinine coefficient of the adult dog.

E. S.

**Is Cystine Synthesised in the Animal Body?** J. A. MULDON, G. J. SHIPLE, and C. P. SHERWIN (*Proc. Soc. Exp. Biol. Med.*, 1922, 20, 46—47).—Bromobenzene, which in the case of

Dogs can be detoxicated by combination with cystine, the amino-group of which is then acetylated, was fed to dogs in conjunction with a carbohydrate diet, and with sodium sulphate, taurine, calcium sulphate, sodium thiocyanate, and aminoethyl mercaptan; detoxication by cystine did not result. The addition of nitrogen in the form of ammonium acetate or gelatin also gave negative results.

## CHEMICAL ABSTRACTS.

**Weight of Microscopic Objects.** [Herring Spermatozoon.]

F. STEUDEL (*Z. physiol. Chem.*, 1923, 130, 136—143).—The following values are arrived at. Weight of one herring spermatozoon,  $1.53 \times 10^{-11}$  mg. Dry weight,  $0.29 \times 10^{-11}$  mg. Nucleic acid content,  $0.12 \times 10^{-11}$  mg. Average weight of herring ovum, 0.923 mg., containing approximately 71.7% of water and 28.3% of dry matter.

W. O. K.

**The Hormone of the Placenta and of the Corpus Luteum and the Lipoids of the Corpus Luteum.** SIGMUND FRÄNKEL and MARIA FONDA (*Biochem. Z.*, 1923, 141, 379—393).—The active substance promoting sexual development in young dogs found by Herrmann (*Monatsh. Geburts. und Gynäkol.*, 1915, 41, 1) in the placenta has been isolated both from the placenta and corpus luteum, and the lipoids of the latter have been investigated. The active principle was obtained from the acetone extract of the ether-soluble portion of the finely minced dry tissues, and distilled in a high vacuum. It was isolated as a viscous, light yellow syrup boiling at  $194^{\circ}/0.064$  mm. Elementary analyses and molecular weight determinations indicate the formula  $C_{35}H_{55}O_2$ . It forms a tetrabromide,  $C_{32}H_{52}O_2Br_4$ , when treated with a solution of bromine in glacial acetic acid. The phenylhydrazone,  $C_{38}H_{58}ON_2$ , a dark orange-red syrup; the acetylphenylhydrazone,  $C_{40}H_{60}O_2N_2$ , a reddish-brown syrup; the oxime,  $C_{35}H_{53}O_2N$ ; the benzenesulphonate of the tetrabromide,  $C_{38}H_{56}O_4Br_4S$ ; the benzoate,  $C_{38}H_{56}O_3$ , and the sodium derivative,  $(C_{32}H_{51}O_2)_2Ba$ , are also described, but none was obtained in a crystalline condition. It is concluded that two unsaturated linkings, a hydroxyl and a carbonyl grouping are present. The distilled product was optically inactive in methyl alcohol and lost some of its activity during distillation. In the product from the chloroform extract of the corpus luteum, there were found, in addition to the active substance, cephalin, lecithin, the ester of dilignoceryl-*N*-diglucosaminomonomosphoric acid, cholesterol, cholesterol ester, glyceryl tripalmitate, free myristic acid, and a galactoside containing nitrogen and phosphorus.

J. P.

**The Ferments of the Hen's Egg.** TORAO KOGA (*Biochem. Z.*, 1923, 141, 430—446).

—Egg-yolk is richer in diastase than egg-white, but both yolk and white diastase increase in quantity during the development of the embryo chick. Egg diastase shows an increased activity in the presence of sodium chloride and, more especially, of blood-serum. Lipases are represented by mono- and di-esterase in the yolk and to a much less extent in the white, and

by tributyrase in a reverse distribution. The latter is unstable to quinine but stable to atoxyl, and diminishes in amount during development whilst the former remains constant. In addition to autolytic enzymes, egg-white contains an erepsin and a fibrin-splitting enzyme. In the yolk, salicylase and histozym are present, but both disappear during development. An oxydase is present in the white which does not act on tyrosine, but forms a brown pigment with pyrocatechol, adrenaline, and dihydroxyphenyl-alanine.

J. P.

**The Proteolytic Enzyme in the Mucous Membrane of the Small Intestine of the Ox.** S. G. HEDIN (*Z. physiol. Chem.*, 1923, 130, 45—54).—If the mucous membrane of the small intestine of the ox is treated at 37° with weak acetic acid of  $p_H$  5.1, a solution is obtained which hydrolyses genuine protein (except unheated serum-albumin), and peptone best in alkaline solution, e. g., it hydrolyses casein best at  $p_H$  9. As the action of this enzyme on casein or peptone is not inhibited appreciably by serum-albumin it must be practically free from trypsin. No enzyme acting best in acid solution appeared to be present, nor could the presence of erepsin be detected.

W. O. K.

**The Chemical Regulation of the Activities of the Human Kidney.** E. F. ADOLPH (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, 63, 432—433).—Hypertonic solutions of substances not changed in metabolism (e. g., sucrose) caused excessive excretion of water by the kidneys, but only the substance ingested was excreted in this excess of water at a rate much above the normal; little but water was excreted at an abnormal rate in water diuresis. Slight but prolonged augmentation of water excretion was caused by Locke's solution and isotonic sodium chloride; rapid diuresis by isotonic potassium chloride and urea; and no increment by isotonic calcium chloride.

CHEMICAL ABSTRACTS.

**The Action of Quinine and Atoxyl on the Lipase of the Kidney.** P. RONA and H. E. HAAS (*Biochem. Z.*, 1923, 141, 222—235).—A Ringer extract of fresh kidney contains a non-dialysable lipase, with an optimum range of action lying between  $p_H$  7 and 8, which in its general properties is identical with blood lipase. Its lipolytic action on tributyrin proceeds as a unimolecular reaction. Kidney lipase is not affected by quinine, but is very susceptible to inhibition by atoxyl. If the logarithm of the atoxyl concentration be plotted against that of the hydrolysis constant, a curve similar to that of a dissociation curve is obtained. The atoxyl inactivation is reversible. Unlike liver lipase, kidney lipase is not protected against atoxyl by the presence of blood-serum. The reactions of the new lipase to quinine and atoxyl therefore serve to differentiate it from all other lipases.

J. P.

**The Chemistry of the Pancreas.** LUDWIG PETSCHACHER (*Biochem. Z.*, 1923, 141, 100—120).—Two kg. of horse pancreas were freed from fat, finely divided, and put through a lengthy series of fractional alcoholic and aqueous extractions and pre-

precipitations, for the exact details of which the original must be consulted. The examination of the various fractions has been only partly completed, and the present results are concerned with two of these. 0.5 G. of a substance, of the formula  $C_{14}H_{31}O_5N_3$ , was obtained in the form of fine, short, white prisms, m. p.  $265^\circ$ , and was slightly levorotatory. It was neutral to litmus and gave negative Millon, xanthoproteic, Mörner, and glyoxylic acid reactions. Injected intravenously into dogs, it produced, in from two to four hours, an increase in blood-sugar. This effect was most marked with small doses. From another fraction L-leucine was isolated in an impure condition. Its intravenous injection produced a lowering of blood-sugar amounting to 30%. Control injections of pure L-leucine (Grübler) had a marked effect in increasing the blood-sugar. It is concluded that the leucine isolated from the pancreas contained as impurity a substance capable of lowering the blood-sugar. The injection of the two fractions investigated had no effect on the animal other than the alteration of the blood-sugar.

J. P.

**Is the Pentose of the Nucleotides Formed under the Action of Insulin?** C. BERKELEY (*Nature*, 1923, **112**, 724—725).—Winter and Smith (this vol., i, 727) having observed that the blood and certain tissues of the rabbit contain, after injection of insulin, a substance which reacts as a carbohydrate with  $\alpha$ -naphthol, but has no reducing action on copper salts even after acid hydrolysis, suggest in effect that this unidentified carbohydrate substance is formed from glucose under the influence of insulin. If this is so, it should be present in normal blood but absent from that of diabetics. It is suggested that the substance may be a pentose nucleotide, such as have been found to be distributed through a wide range of animal tissues; nucleotides give the  $\alpha$ -naphthol reaction, and unsuitable conditions of hydrolysis may cause the pentose to be overlooked. From experiments on the islet gland in a typical teleost fish, the author infers that the general high pentose content of the pancreas in mammals is due mainly to the presence of the isles of Langerhans. An hypothesis indicating a connexion between the production of insulin and the high concentration of pentose compounds in the islet tissue is outlined.

A. A. E.

**Relation between Innervation and Chemical Composition of Striped Muscle. I. Creatine Content in Hyperinnervation.** J. G. DUSSE DE BARENNE, and D. G. COHEN T'ERVAERT. (*Pflüger's Archiv*, 1922, **195**, 370—389; from *Chem. Zentr.*, 1923, **iii**, 321).—The creatine content of the muscle of cats is unchanged in rigor due to removal of the brain. Increase in creatine content occurs in phasal innervation superimposed on rigor due to removal of the brain.

G. W. R.

**Hydrolysis of the Muscle Protein of *Cryptobranchus japonicus*, Hoev.** I. SHIGEO SUGA (*J. Pharm. Soc. Japan*, 1923, No. 497, 588—592).—The muscle protein of *Cryptobranchus*

*japonicus*, Hœv., was hydrolysed by boiling with ten times its weight of 33% sulphuric acid for fourteen hours and the amino-acids formed were separated and determined by the methods of Kossel and of Kutscher. One hundred g. of the water-insoluble dried flesh (nitrogen content 13.65%) gave 6.69 g. of arginine, 2.29 g. of histidine, and 7.41 g. of lysine.

K. K.

**Composition of the Cartilage of an Invertebrate Animal, *Limulus*.** A. P. MATHEWS (*Z. physiol. Chem.*, 1923, **130**, 169—175).—The entosternite of the cartilage of *Limulus* is a mixture of cartilaginous and fibrous connective cells, as shown by its chemical composition. It is a typical protein, with very little prosthetic substance, containing no gelatin and only a small quantity, 1—2%, of chondroitinsulphuric acid. W. O. K.

**The Concentration of Protein in Tissues.** E. J. COHN (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, **63**, 430—431).—The relationship of water, electrolytes, and proteins in animal tissues is discussed from the point of view of physical chemistry. The variations among species of these cell constituents agree with the theories of Donnan and of Loeb on membrane equilibrium. The concentration of such dissociable, non-diffusible contents of cells as the proteins must lead not only to the loss of water, but also to the loss of diffusible electrolytes with which the proteins are in equilibrium. CHEMICAL ABSTRACTS.

**The Normal Content of Arsenic in the Human Body.** O. BILLETER and E. MARFURT (*Helv. Chim. Acta*, 1923, **6**, 780—784).—Using the method already described (this vol., ii, 786), the normal content of arsenic in different parts of the human body in subjects of different ages was determined. An appreciable, fairly constant quantity of arsenic was always found, the mean value being about 0.0103 mg. per 100 g., with an excess of 0.0032 mg. in the thyroid gland and a deficit of 0.0019 mg. in the spleen. In the newly-born, the proportion is considerably less, but in elderly people it is above the average, and a specially high amount was found in the nails of an old man. E. H. R.

**The Nitrogen Compounds of Skimmed Milk Cheese.** E. WINTERSTEIN and O. HUPPERT (*Biochem. Z.*, 1923, **141**, 193—221).—Details are given of the qualitative and quantitative distribution of the nitrogen present in skimmed milk cheeses of various ages, and these are compared with fatty cheeses (Emmentaler, Cheddar). The former are found to have a higher water, ash, and ammonia content than the latter. The skimmed milk cheeses do not ripen so rapidly as the fatty varieties, which is reflected in the higher amino-acid content of the latter (100 to 150% greater) as compared with the former. The total nitrogen of the skimmed milk cheeses, freed from water and fat and exclusive of the ash, varied between 13.4 and 13.9% and the total protein nitrogen between 11.4 and 12.5%. The basic and amino-acid nitrogen, although low, was very variable, and, in general, the nitrogen precipitable by phosphotungstic acid variable inversely as that of the amino-acids. In both fatty and

skimmed milk cheeses, the ripening process is accompanied by the formation of valine, leucine, isoleucine, glycine, alanine, phenylalanine, proline, aspartic acid, and glutamic acid. Notably the hexone bases are absent or present only in minimal amount in the skimmed milk cheeses, but they contain considerable quantities of polypeptides yielding bases on hydrolysis. Caseoglobulin, tyroalbumin, and tyrocasein are also present. The xanthidrol reaction failed to reveal the presence of urea. J. P.

**Excretion of Lactic Acid in Urine.** F. KNOOP and H. JOST (*Z. physiol. Chem.*, 1923, 130, 338—349).—Lactic acid is excreted in the urine of dogs after ingestion of propionic acid, butyric acid, hydroxybutyric acid, and, to a small extent, malonic acid. The mechanism of the formation of lactic acid under these conditions is discussed. W. O. K.

**Synthesis of Hippuric Acid in the Animal Organism. V. The Influence of Amino-acids and Related Substances on the Synthesis and Rate of Elimination of Hippuric Acid after the Administration of Benzoate.** WENDELL H. GRIFFITH and HOWARD B. LEWIS (*J. Biol. Chem.*, 1923, 57, 1—24).—The rate of excretion of hippuric acid following the oral administration of sodium benzoate is decidedly increased when glycine is administered simultaneously with the benzoate, thus indicating an increased rate of synthesis of hippuric acid in the presence of large amounts of glycine. No increased rate of elimination was observed when other amino-acids, glycollic acid, glycollaldehyde, dextrose, urea, or sodium acetate were used in place of glycine. Apparently none of these substances is a readily available precursor of glycine. E. S.

**Can Aliphatic Diamines be Obtained from Normal and Nephritic Urine by Means of Picric Acid and Sodium Chloride?** R. SCHÜLER and F. THIELMANN (*Z. Biol.*, 1923, 79, 139—144).—The precipitate produced in normal urines by 1% aqueous picric acid and saturated sodium chloride, and supposed by Bergell (this vol., i, 1155) to contain uripicric acid (1 mol. of uric acid + 1 mol. of picric acid) and aliphatic diamines, is found to consist of sodium picrate, creatinine, uric acid, and pigments. The precipitate produced by substituting saturated potassium chloride for sodium chloride consists of potassium picrate and creatinine, which is quantitatively precipitated, together with small quantities of uric acid. Precipitates of similar composition varying only in quantity are obtained from various nephritic urines. J. P.

**A Special Group of Enteroliths from Man; Choleic Acid Stones.** CARL TH. MORNER (*Z. physiol. Chem.*, 1923, 130, 24—33).—A large enterolith was found to have the following composition: organic material soluble in alcohol, 76.34%; organic material insoluble in alcohol, 8.46%; mineral matter, 2.42%; water, 12.78%. The organic material did not contain cholesterol, glycolic acid, cholic acid, or lithocholic acid, but consisted essentially

of choleic acid,  $C_{24}H_{40}O_2$ . The following derivatives were prepared: acetylcholeic acid, m. p. 142–143°, xylene-choleic acid, m. p. 181°, and stearin-choleic acid, m. p. 188°. W. O. K.

**Fat Metabolism in Avitaminosis. I. The Total Fat and Cholesterol Contents of the Body on Normal and Vitamin-free Diets.** KAZUO ASADA (*Biochem. Z.*, 1923, 141, 166–186).—Rats kept on vitamin-free diets showed a diminution of total and neutral body fat when compared with normal controls. The fat content in vitamin-fed animals kept on various diets diminished in the order of dieting given: fat > carbohydrate > mixed > protein, whilst in the avitaminosed animals the order was: mixed > carbohydrate > fat > protein. In avitaminosis, the total cholesterol underwent less diminution than did the fat. The order of diminution for the various diets employed was: in the vitamin-fed animal, fat > mixed > carbohydrate > protein; in the avitaminosed animal, mixed > carbohydrate > fat > protein. The order of the length of life on various vitamin-free diets was: mixed > carbohydrate > fat > protein. Under normal dietetic conditions, no diminution of life period was observed except when the rats were kept on a starch or protein diet. In general, avitaminosis is associated with an increased blood-fat content, a diminished capacity to store fat, and an increase in its rate of oxidation. J. P.

**The Fat Content of the Blood in Avitaminosis.** J. A. COLLAZO and GOMEZ BOSCH (*Biochem. Z.*, 1923, 141, 370–378).—In avitaminosed dogs the total blood-fat and cholesterol undergo a marked increase, but again fall in the later stages without returning to normal values before death. The blood phosphatides show little alteration, but may diminish slightly in the late stages of avitaminosis. On doubling the amount of fat in the diet of avitaminosed dogs, the period of increased blood-fat is of longer duration than that produced in normal animals by similar methods. The hyperlipæmia in avitaminosis is associated with a diminution in the total body fat (cf. Asada, preceding abstract). J. P.

**Glycolysis in Diabetic and Non-diabetic Blood.** W. DENIS and UPTON GILES (*J. Biol. Chem.*, 1923, 56, 739–744).—Glycolysis is much more active in normal blood than in blood from patients with severe diabetes. It is suggested in explanation that the glycolytic enzyme attacks  $\gamma$ -glucose, which is present in normal, and practically absent from diabetic, blood, but is without action on  $\alpha$ - $\beta$ -glucose (cf. Forrest, Smith, and Winter, this vol., i, 513). E. S.

**The Behaviour of the Urea and Non-urea Fraction of the Residual Nitrogen in Heart and Kidney Affections.** HUGO PRIBRAM and OTTO KLEIN (*Biochem. Z.*, 1923, 141, 488–499).—The urea-nitrogen, the non-urea-nitrogen, and the "double nitrogen" (difference in the nitrogen of the filtrates after precipitation with trichloroacetic and with phosphomolybdic acids) of blood, have been determined as ratios of the total residual nitrogen in cases of heart and kidney affections and in normals. The "double

nitrogen" of the non-urea fraction is a measure of the protein breakdown and may vary markedly with regard to the residual nitrogen. In the conditions studied, increased degradation of tissue proteins produces a high "double nitrogen" value and the ratio of the urea nitrogen to the residual nitrogen is lessened. In kidney and heart affections, oliguria and cedema are associated with an increase in urea nitrogen, whilst in polyuria and cedema drainage the urea fraction is diminished and the non-urea and double nitrogen fraction increases. The ratio of the urea nitrogen to the residual nitrogen is increased in renal insufficiency, but in the late stages the other fractions increase whilst the urea diminishes. The fractional examination of the residual nitrogen must be modified according to the protein content of the serum. J. P.

**Syphilis. IV. The Arsenic Content of the Blood at Various Intervals after Intravenous Injection of Salvarsan.** J. A. FORDYCE, ISADORE ROSEN, and C. N. MYERS (*Amer. J. Syphilis*, 1923, 7, 225—286).—Immediately after the injection, 60% of the arsenic has been localised outside of the blood-stream, and this is the time of maximum concentration of arsenic in the blood, 4.21 mg. of elementary arsenic being present in 100 g. of dried material. The rate of division of arsenic between blood and tissues varies in different individuals. Persons with an arsenic idiosyncrasy show abnormal values for the arsenic in the blood.

CHEMICAL ABSTRACTS.

**Neurosyphilis. I. Arsenic Content of the Spinal Fluid after the Intravenous Administration of Silver Salvarsan.** L. H. CORNWALL and C. N. MYERS (*Amer. J. Syphilis*, 1923, 7, 287—317).—Within two hours of the intravenous injection of silver salvarsan, arsenic may be found in the spinal fluid in amounts as large as 143 mg. per 100 g. of dried material. Usually the amount present decreases after the first two hours, rises slightly between twenty-four and forty-eight hours, and reaches a new high point at seventy-two hours, when as much as 192 mg. per 100 g. of material may be present.

CHEMICAL ABSTRACTS.

**Alkalosis versus Abnormal Sodium-ion Concentration as a Cause of Tetany.** W. DENIS and L. VON MEYSENBUG [with JULIA GODDARD] (*J. Biol. Chem.*, 1923, 57, 47—63).—The tetany produced in dogs by excessive injections of sodium hydrogen carbonate is due to an abnormal  $\text{H}_2\text{CO}_3/\text{NaHCO}_3$  ratio rather than to poisoning by sodium-ions. Injections of sodium chloride or sodium sulphate, whilst producing convulsions, do not increase the irritability of the nerves; with sodium hydrogen carbonate, on the other hand, both these effects are produced. E. S.

**The Fate of Sodium Thiosulphate in the Organism.** WILHELM NYIRI (*Biochem. Z.*, 1923, 141, 160—165).—That portion of sodium thiosulphate, administered intravenously or orally, which is not excreted unchanged by the kidney, is oxidised completely to sulphuric acid and is present in the urine as sodium sulphate.

J. P.

**A Pharmacological Comparison of Six Alcohols, Singly and in Admixture, on *Paramacium*.** CHARLES E. BILLS (*J. Pharm. Exp. Ther.*, 1923, 22, 49—57).—The narcotising and toxic effect on *Paramacium caudatum* of methyl, ethyl, propyl, isopropyl, butyl, and isobutyl alcohols was examined. The criterion of narcotisation adopted was the inability of the organisms to rise to the surface of the liquid. It was found that both toxicity and narcotising power increase progressively with the molecular weight. The margin between narcotising and toxic concentrations is greater in the case of propyl alcohol than in the case of either ethyl or butyl alcohols. isopropyl and isobutyl alcohols are less toxic than their normal isomerides, although isobutyl alcohol is more narcotic than *n*-butyl alcohol. When mixed the alcohols antagonise each other in narcotising effect.

C. R. H.

**Formation of Dextrose from Alanine and from Lactic and Pyruvic Acids.** E. AUBEL and R. WURMSER (*Compt. rend.*, 1923, 177, 836—837).—Since, with phloridzinised dogs, alanine and lactic acid give their own weight of extra dextrose, whilst pyruvic acid gives less than its own weight, the latter substance, in preventing acetonuria in dogs by formation of dextrose, should be required in a larger proportion than the two former substances. It is actually found that 92% of alanine or of lactic acid but only 80% of pyruvic acid, is thus converted into dextrose, this being due to the greater ease with which pyruvic acid is oxidised in the animal organism. It is concluded that alanine and the above acids are not transformed directly into dextrose but that intermediate compounds are not only formed, but also should be discoverable.

E. E. T.

**The Behaviour of Fatty Aromatic Ketones in the Animal Body.** H. THEIRFELDER and K. DAIBER (*Z. physiol. Chem.*, 1923, 133, 380—396).—After subcutaneous injection of acetophenone into rabbits, 35.7% is reduced to the carbinol and excreted as the paired glycuronic acid, whilst 24.3% is oxidised to benzoic acid and excreted as hippuric acid. Forty % is completely decomposed. Ethylbenzene is eliminated as hippuric acid, phenylmethylcarbinol and mandelic acid (isolated as the cadmium salt). Various alkyl ketones investigated, propiophenone, butyrophenone, benzyl propyl ketone, and benzyl isopropyl ketone, are reduced to the carbinol and also are oxidised; benzyl isopropyl ketone yields phenylacetic acid.

W. O. K.

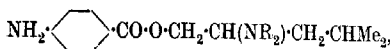
**The Supposed Colloidal Character of Solutions of Chloroform and Some of its Related Compounds.** PANCHANAN BOSE (*Biochem. Z.*, 1923, 141, 269—273).—By subjecting aqueous solutions of chloroform, dichloromethane, tetrachloromethane, ethylene dichloride, and *s*-tetrachloroethane to the Tyndall test, to ultra-microscopic examination and to ultra-filtration, and by measuring their depression of freezing point and rates of diffusion into gelatin and through membranes, it is shown that these halogen derivatives are present in a state of molecular dispersal and not in the colloidal condition as supposed in Traube's theory of narcosis.

J. P.

**The Physiological Action of Proteinogenic Amines. VIII. The Local Anæsthetic and Narcotic Action of Phenylethylamine and Some of its Derivatives.** J. ABELIN (*Biochem. Z.*, 1923, 141, 453—470).—Phenylethylamine has a strong local anæsthetic action on muscle-nerve preparations, and in concentrations of  $M/200$  to  $M/500$  acts as a narcotic on frog larvæ. The introduction of a para-hydroxyl group, as in tyramine, increases both actions. Hordenine has but slight narcotic properties. The activity of phenylethylamine derivatives varies with the  $p_n$ , being most marked at  $p_n$  8.4 to 8.5 and much less in acid solutions. The increased imbibition of water by gelatin in the presence of phenylethylamine is greatly diminished in neutral and acid solutions.

J. P.

**The Relationship between Chemical Constitution and Local Anæsthetic Action in the Case of *N*-Alkyl Derivatives of the Leucinol Ester of *p*-Aminobenzoic Acid.** HANS GRAF (*Arch. exp. Path. Pharm.*, 1923, 99, 315—345).—The first part of the paper is a theoretical discussion of the relationship between chemical constitution and local anæsthetic action with special reference to the cocaine group. The experimental part deals with the investigation of the *N*-dialkyl derivatives of the *p*-aminobenzoic ester of isobutylaminoethyl alcohol ("leucinol"), being substances of the type



and also of the *N*-piperidyl derivative. Of the whole series investigated, the *N*-diethyl derivative was the only one which seemed promising from the practical point of view. Its anæsthetic power approximates to that of cocaine, whilst its toxicity is intermediate between those of cocaine and novocaine.

C. R. H.

**The Central Influence of Atropine and Hyoscine on the Heart Rate.** W. J. R. HEINEKAMP (*J. Lab. Clin. Med.*, 1922, 1, 104—111).—Small doses of atropine (0.0003 g. in dogs and 0.001 g. in man) produce inhibition of the heart owing to direct stimulation of the cardio-inhibitory centre. Hyoscine exerts a similar action to that of atropine on the medulla of *Pseudomys roosii*, except that the primary stimulation is followed by depression.

CHEMICAL ABSTRACTS.

**Difference in Activity of Optical Isomerides (*l*-Cocaine and *d*-Cocaine).** R. GOTTLIEB (*Z. physiol. Chem.*, 1923, 130, 74—379).—On subcutaneous injection, *d*- $\psi$ -cocaine is at most only one-half as poisonous as *l*- $\psi$ -cocaine for the central nervous system of the frog, mouse, or cat. 0.15—0.18 Mg. of *l*-cocaine is toxic for 1 g. mouse whilst at least 2 mg. of the *d*-cocaine are required. It is considered that detoxication of the *d*-form occurs more quickly.

W. O. K.

**The Action of Morphine, Codeine, and apoMorphine as Shown by Perfusion of the Medulla of the Terrapin (*Pseudomys troosti*).** W. J. R. HEINEKAMP (*J. Lab. Clin. Med.*, 1923, 8, 165—169).—Morphine sulphate when perfused through the medulla of the terrapin produces inhibition of the heart, owing to its products of oxidation, since morphine oxidised in vitro with nitric acid when perfused exerts a quicker and more powerful stimulating action than morphine itself. Codeine exerts no influence on the medulla, probably because of the presence of a methoxyl group. However, when oxidised it too has a powerful stimulating effect. apoMorphine first stimulates and then paralyses the medulla. Solutions which have been exposed to air and hence oxidised are ineffective.

CHEMICAL ABSTRACTS.

**Increase in the Toxic Action of Carbon Disulphide-Hydrogen Sulphide Gaseous Mixtures.** RICHARD FISCHER (*Biochem. Z.*, 1923, 141, 540—544).—With the view of determining if a mixture of two toxic gases has a greater toxicity than that of the sum of its separate components, dogs were subjected to the action of varying concentrations of hydrogen sulphide, carbon disulphide, and a mixture of both gases. In general, no increased toxicity was noted, the effects being those produced by each component in corresponding concentration.

J. P.

**The Mechanism of the Action of Arsenic on Protoplasm.** C. VOEGTLIN, H. A. DYER, and C. S. LEONARD (*U.S. Pub. Health Repts.*, 1923, 38, 1882—1912).—Reduced glutathione, thioglycollic acid,  $\alpha$ -thiolactic acid, glycylcysteine, and thiosalicylic acid counteract the toxic action of arsenic compounds of the structure  $RA_sO$  on trypanosomes in vitro and in the blood of rats, whilst disulphides,  $R\cdot S\cdot S\cdot R$ , are much less, if at all, effective. The amount of the compound (possibly glutathione) containing an  $\cdot SH$  group, present in all cells, is thereby prevented from falling below the physiological requirement owing to its chemical interaction with the arsenic compound. Glutathione and some other analogous compounds are concerned in certain biological oxidations and reductions.

3-Amino-4-hydroxyphenylarsino-bismonothioglycollic acid is prepared in 94.2% purity by heating on a water-bath a mixture of 7 g. of 3-amino-4-hydroxyphenylarsenious oxide hydrochloride and 11 g. of thioglycollic acid, drying the gummy mass in a desiccator, washing it with ethyl ether, and dissolving in absolute ethyl alcohol. After removal of the alcohol in a vacuum, the residue is again washed with ethyl ether, dried in a desiccator, and pulverised. The above theory of the action of arsenic is supported by the fact that in equimolecular doses it shows a marked delay in parasiticial action as compared with arsenoxide.

CHEMICAL ABSTRACTS.

## Chemistry of Vegetable Physiology and Agriculture.

**Reducing Action of Micro-organisms on Ammonium Molybdate.** V. E. LEVINE and H. M. JAHR (*Abstracts Bact.*, 1921, 5, 4—5).—Bacteria growing in peptone broth containing ammonium molybdate reduce that compound with the production of an intense blue colour. Sterile dextrose peptone broth produces this reduction at a temperature of 37.5° but not at room temperature. Peptone broth containing 1% of lactose and 1% of ammonium molybdate is reduced only in the presence of micro-organisms. No relationship exists between reduction and fermentation. Living yeast-cells also produce the reduction. Both bacteria and yeast secrete reductase as an endocellular enzyme; the reduction is due partly to this enzyme and partly to the metabolic products of the organisms. Low concentrations of ammonium molybdate do not retard bacterial growth; the degree of retardation, or even complete inhibition, produced by a relatively high concentration (1%) varies with the species.

CHEMICAL ABSTRACTS.

**The Minimum Concentration of Oxygen for Luminescence by Luminous Bacteria.** E. NEWTON HARVEY and THOMAS F. MORRISON (*J. Gen. Physiol.*, 1923, 6, 13—19).—A method is described for estimating the minimum concentration of oxygen which is necessary to produce a perceptible luminescence in luminous bacteria. Using this method, a value equivalent to an oxygen pressure of about 0.005 mm. of mercury was found. E. S.

**The Formation of Acetaldehyde during the Fermentation of Lævulose, Galactose, Sucrose, Maltose, and Lactose by *Bacillus coli* and *B. lactis aerogenes*.** K. NAGAI (*Biochem. Z.*, 1923, 141, 261—265).—Lævulose, galactose, sucrose, maltose, and lactose all yield acetaldehyde when fermented at 37° by cultures of *B. coli* and *B. lactis aerogenes* in the presence of yeast-water, peptone, and calcium carbonate. Variable yields from 0.5% to 7% of aldehyde, isolated as the bisulphite compound, were obtained.

J. P.

**The Formation of Acetaldehyde during the Bacterial Degradation of Carbohydrate Acids and Related Acids.** K. NAGAI (*Biochem. Z.*, 1923, 141, 266—268).—Malic, *dl*-lactic, *d*-tartaric, *d*-glyceric, and *d*-gluconic acids, fermented by cultures of *Bacillus coli* and *B. lactis aerogenes*, yield appreciable quantities of acetaldehyde in the presence of yeast-water, ammonium sulphate, and calcium carbonate. The presence of sodium sulphite in the culture is necessary. In its absence no aldehyde was detected.

J. P.

**Butylene Glycol Fermentation of Calcium Lactate by Bacteria of the *B. subtilis* group.** M. LEMOIGNE (*Compt. rend.*, 1923, 177, 652—654).—Lactic acid, like sugar, is decomposed by bacilli of the *Bacillus subtilis* group, with formation of butylene

glycol ( $\beta$ -dihydroxybutane) and  $\gamma$ -hydroxybutan- $\beta$ -one (acetyl-methylcarbinol). Owing to the great stability of lactic acid, these products are formed only slowly, so that they are only detectable in old cultures in which oxidative and synthetic processes (which cause their disappearance as soon as they are formed) are reduced to a minimum.

E. E. T.

**Influence of Concentration of Sugar in Media on Activity of Nitrogen-fixing Bacteria.** G. TRUFFAUT and N. BEZSSONOFF (*Compt. rend.*, 1923, **177**, 649—652).—In a nitrogen-free medium (Hutchinson liquid), the development of aerobic soil bacteria is favoured by concentrations of sugar of the order of 1:1000, rather than by higher concentrations, the converse being true of the corresponding anaerobic bacilli. The aerobic nitrogen-fixing bacilli (*Bacillus Truffauti* and *B. azotobacter agilis*) act best with feeble concentrations of sugar than have usually been employed. In the case, however, of the anaerobic *Clostridium Pastorianum*, though cultivated in symbiotic union with the (aerobic)  $\beta$ -bacillus, the fixation of nitrogen is not appreciably affected by the concentration of sugar.

E. E. T.

**The rôle of Vitamins and Avitaminosis in Microbiology. Avitaminosis and Increase of Virulence.** ALBERTO ASCOLI (*Z. physiol. Chem.*, 1923, **130**, 259—269).—Pathogenic bacteria grown in a vitamin-free medium increase in virulence. A similar increase in virulence *in vivo* explains the increased virulence of infection in animals suffering from avitaminosis. The effective agent, "exaltin," appears to be a dialysable substance.

W. O. K.

**The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. I. The Behaviour of Dextrose. II. The Behaviour of the Monosaccharides.** HARRY LUNDIN (*Biochem. Z.*, 1923, **141**, 310—341, 342—369).—A detailed investigation of the course of the fermentative action of yeast on dextrose, laevulose, and galactose at temperatures varying from 16° to 20°, and in the absence of a source of nitrogen in the fermentation mixtures. The experiments were conducted both under conditions assuring excess of oxygen (by shaking with the gas) and under normal conditions with access of air only. Under these conditions galactose was only slightly fermented, and in general the results given by dextrose and laevulose, which are both rapidly fermented, were similar. No increase in the number of yeast-cells was observed, but the total cell mass underwent a 60% increase as estimated from the dried cell residue. This increase did not affect the cell proteins. None of the usual by-products of alcoholic fermentation was formed nor was the production of fat or acetaldehyde noted. Both in the presence and in the absence of excess of oxygen assimilation of the sugar to higher carbohydrates occurred, and evidence is available to show that this process takes place with the intermediate formation of alcohol and involves the liberation of one-third of the total energy of the

assimilated sugar, the remaining two-thirds being utilised by the complex assimilatory products. These are solely of a carbohydrate nature and consist in part of a readily hydrolysable form—glycogen, and a form soluble to a large extent in 3% hydrochloric acid, but not hydrolysed by this strength of acid. The two forms are produced in equal proportions, but the easily hydrolysable glycogen alone may be subsequently utilised by the yeast-cells as a source of energy when the fermentable sugar in the solution is exhausted. This utilisation of assimilated glycogen is markedly increased in the presence of excess of oxygen. The assimilatory processes are independent of the rate of fermentation. The author regards his results as opposing the glycogen fermentation theory of Grüss (*Zeit. ges. Brauwesen*, 1904, 27) and as favouring Laquer's views (*A.*, 1922, i, 1089) on the oxidation of dextrose through preliminary transformation into a readily oxidisable form. J. P.

**The Action of Metallic Salts on the Course of Alcoholic Fermentation.** ALBERT VON MAY (*Biochem. Z.*, 1923, 141, 47—457).—The observations of Kostytshev (*A.*, 1912, ii, 589; 1921, i, 149), that during the fermentation of sugar by yeast in the presence of cadmium and zinc salts a large proportion of the sugar disappears without forming known condensation or degradation products, are due to the difficulty of estimating sugar by reduction methods in the presence of yeast-proteins. If these be precipitated, the presence of the unchanged sugar may be demonstrated both polarimetrically and by reduction methods. The increased aldehyde formation also observed by Kostytshev is produced by the addition of other salts, notably those of barium, calcium, glucinum, magnesium, and iron, and to a less extent by nickel, tin, lead, aluminium, and thallium salts. J. P.

**The Specific Action of Ferments. Is it Possible by Means of Ferments to Determine whether Amino-acids of Known Configuration are Present in Nature, Particularly as Constituents of Protein?** EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 130, 205—207).—Polypeptides have been synthesised containing  $\alpha$ -*dl*-aminoheptonic acid,  $\alpha$ -*dl*-amino-octic acid, and  $\alpha$ -*dl*-aminomyristic acid. These amino-acids are not known to occur naturally. The racemic polypeptides are hydrolysed asymmetrically by yeast-cells, indicating that it is not the whole structure of the protein but only a particular group that determines whether it will be attacked by the enzymes. W. O. K.

**The Behaviour of Pyrimidine Derivatives in the Organism.**  
**I. The Action of Yeast on Pyrimidine Derivatives.** AMANDUS HAHN and WOLFGANG LINTZEL (*Z. Biol.*, 1923, 79, 179—190).—Living yeast-cells in the presence of sucrose, and cell-free yeast extracts deaminate cytosine at room temperature with formation of uracil. In the former case, the liberated ammonia serves the cells as a source of nitrogen, and in the latter case the deamination, which is quantitative, causes the solution to become alkaline.

Uracil and thymine are not affected by yeast or by yeast extracts even when the solutions are aerated. The deaminising action of yeast extracts on cytosine is lost on boiling. It is concluded that a cytosine deaminase is present in yeast.

J. P.

**Biochemistry of the Germination of Cereal Grains.** HANS LOIBL (*Z. ges. Brauwesen*, 1923, 46, 30—35, 37—41, 45—48, 53—56, 61—67, 69—72; from *Chem. Zentr.*, 1923, iii, 396—397).—The increase in soluble substances in the endosperm of germinating cereal seeds is the result of degradation of reserve materials. The starch content decreases partly through respiration and partly through the formation of soluble carbohydrates. An increase in soluble carbohydrates, reducing sugars, and sucrose occurs. The increase in soluble pentosans during germination is due to hydrolysis of the hemicelluloses of the cell-walls. There is no appreciable increase in total pentosans and total crude fibre. Total nitrogen, coagulable nitrogen, and nitrogen titratable by formaldehyde all increase. The notable increase in total titratable acidity is mainly due to the change of organic phosphates to inorganic phosphates. There is, however, a slight decrease in hydrogen-ion concentration. Amylase, catalase, peptase, cytase, and phytase show increases, whilst urease shows a decrease.

G. W. R.

**A Method of Simultaneously Studying the Absorption of Oxygen and the Discharge of Carbon Dioxide in Respiration.** D. S. FERNANDES (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 408—419).—A detailed description is given of a thermostatic apparatus for the study of respiratory exchange in plants. The respiratory gases are pumped round a closed circuit; a known quantity of oxygen can be introduced by an electrolytic method, and the carbon dioxide may be estimated by means of baryta.

H. H.

**Comparative Studies on Respiration. XVIII. Respiration and Antagonism in *Elodea canadensis*.** C. J. LYON (*Amer. J. Bot.*, 1921, 8, 458—463).—Working with *Elodea canadensis* it was found that solutions of sodium chloride (0.1M) caused an initial increase in respiration followed by a decrease. Calcium chloride solution (0.07M) caused a decrease in respiration. Respiration remains normal in the presence of sodium chloride and calcium chloride when these salts are present in the molar ratio 99.65 : 0.35. The curve showing the rate of respiration with mixtures of sodium chloride and calcium chloride in varying proportions is unique in that it shows two maxima, one at 99.65 : 0.35, as above, and the other at 98.62 : 1.38. At the latter maximum, respiration is very much increased above normal.

G. W. R.

**Comparative Studies on Respiration. XXII. The Effect of Lactic Acid on the Respiration of Wheat.** EDITH PHILLIPS SMITH (*Amer. J. Bot.*, 1922, 9, 307—310).—In high dilutions such as 0.0025M, lactic acid first increases and then depresses the

rate of production of carbon dioxide of wheat seedlings. With more concentrated solutions the maximum becomes less marked, until finally only a decrease is observed. Recovery occurs even after the rate of respiration has been reduced to 25% of normal by a 2*M*-solution of lactic acid. The effects are believed to be due to a specific action of lactic acid. It is concluded that lactic acid is not an intermediate substance in the metabolism of wheat seedlings.

G. W. R.

**New Method of Proceeding from Carbonic Acid to Formaldehyde. Theory of the Assimilation of Carbon Dioxide.** T. THUNBERG (*Z. physikal. Chem.*, 1923, 106, 306—312).—When basic lead carbonate, preferably in the presence of boric acid, is boiled with hydrogen peroxide and the resulting mixture distilled, the distillate is found to contain formaldehyde. The reaction is carried out by mixing 5 g. of basic lead carbonate with 100 c.c. of distilled water and heating to boiling in a 250 c.c. distilling flask. When 10 c.c. of liquid had distilled over, 50 c.c. of 6% hydrogen peroxide was added slowly and further portions of 10 c.c. of distillate collected in each of which formaldehyde was found. Other carbonates gave negative results. On the basis of this experiment, the author puts forward an hypothesis for the assimilation of carbon dioxide, according to which sunlight decomposes water with the formation of hydrogen and hydrogen peroxide,  $2\text{H}_2\text{O} = \text{H}_2 + \text{H}_2\text{O}_2$ . Then carbon dioxide reacts with hydrogen peroxide and hydrogen to form methylene glycol,  $\text{CO}_2 + \text{H}_2 + \text{H}_2\text{O}_2 = \text{H}_4\text{CO}_2 + \text{O}_2$ , and this compound loses a molecule of water with the formation of formaldehyde,  $\text{H}_4\text{CO}_2 = \text{H}_2\text{O} + \text{HCHO}$ .

J. F. S.

**Theory of the Assimilation of Carbon Dioxide.** FRITZ WEIGERT (*Z. physikal. Chem.*, 1923, 106, 313—323).—A theoretical paper in which the author discusses the hypothesis put forward by Thunberg for the assimilation of carbon dioxide (preceding abstract). The author puts forward the following scheme to represent the mechanism of the assimilation of carbon dioxide.  $2\text{Chlorophyll} + 2h\nu + 2\text{O}_2 = 2\text{Chl}^+ + 2\text{O}_2^-$ ;  $2\text{O}_2^- + 2\text{H}_2\text{O} = 2\text{H} + 2\text{OH}^- + 2\text{O}_2$ ;  $2\text{H} + 2\text{OH}^- + 2\text{Chl}^+ = \text{H}_2 + \text{H}_2\text{O}_2 + 2\text{Chl}$ . These lead to the total equation  $2\text{H}_2\text{O} + 2h\nu = \text{H}_2 + \text{H}_2\text{O}_2$  (1) which is followed by  $\text{CO}_2 + \text{H}_2 + \text{H}_2\text{O}_2 = \text{H}-\text{COH} + \text{H}_2\text{O} + \text{O}_2$  (2). The sum of (1) and (2) give the final equation  $\text{CO}_2 + \text{H}_2\text{O} + 2h\nu = \text{HCHO} + \text{O}_2$ . The reactions are both endothermic,  $2\text{H}_2\text{O} = \text{H}_2 + \text{H}_2\text{O}_2 - 92,000$  cal.  $\text{CO}_2 + \text{H}_2 + \text{H}_2\text{O}_2 = \text{HCOH} + \text{H}_2\text{O} + \text{O}_2 - 18,000$ , consequently the light energy  $2Nh\nu$  must furnish this energy. Calculation shows that this can be done by wave-lengths of 517  $\mu$ . At this wave-length, the radiation is transformed completely into chemical energy in this reaction.

J. F. S.

**A Factor Causing the Assimilation of Calcium.** CHAS. H. LUNT and A. R. WINTER (*Science*, 1923, 57, 717—718).—It is assumed that most of the calcium, however combined, in the cells of green plants is in a highly dispersed form, and is hence better

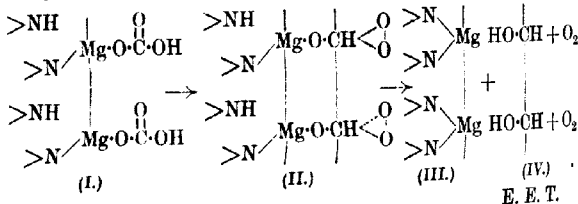
assimilated than the calcium in the dry plant. The cell contents were roughly imitated by a solution containing calcium chloride, sodium phosphate, and starch paste, and fed, with grain and dry timothy hay, to goats. The results are, however, so far inconclusive.

A. A. E.

**The Absorption of Ions by Plants, including Observations on the Effect of Light.** D. R. HOAGLAND and A. R. DAVIS (*J. Gen. Physiol.*, 1923, 6, 47—62).—The absorption of inorganic ions by the fresh-water alga *Nitella* (this vol., i, 882) is favoured by illumination. It is concluded that light supplies the energy necessary for the transference of the ions from a dilute solution into the more concentrated cell sap. The absorption of one ion may be influenced by the presence of another.

E. S.

**Theory of Chlorophyllic Synthesis.** L. MAQUENNE (*Compt. rend.*, 1923, 177, 853—857).—The theories hitherto put forward to account for the synthesis of carbohydrates in plants are unsatisfactory, mainly because they assume formaldehyde to be formed intermediately, whereas its presence in plants has never been indubitably proved. It is now suggested that photosynthesis of carbohydrates is effected through the agency of colloidal chlorophyll, which is assumed to be a polymerised chlorophyll possessing the grouping III, that is, containing quadrivalent magnesium, associated with weakened attachment of metal to nitrogen. Carbonic acid is assumed to combine with III, giving I, which then undergoes isomeric change to give II, this complex losing the oxygen which is characteristic of photosynthesis, being at the same time converted into polymerised (colloidal) chlorophyll (III) and a carbohydrate (IV). The complexity of the latter is determined by the complexity of the polymerised chlorophyll, and this is obviously capable of considerable variation. Thus, if six mono-magnesium complexes are polymerised to give a ring, inositols will result.



E. E. T.

**The Effect on Permeability of Multivalent Kations in Combination with Multivalent Anions.** O. L. RABER (*Amer. J. Bot.*, 1921, 8, 382—385; from *Physiol. Abstr.*, 1923, 8, 315).—Bivalent and trivalent kations in combination with univalent anions produce an initial increase in the electrical resistance of *Laminaria*, but when combined with bivalent or trivalent anions the increase is reduced and may be zero.

W. O. K.

**The Effect on Permeability of (I) the Same Substance as Kation and Anion and (II) Changing the Valency of the Same Ion.** O. L. RABEE (*Amer. J. Bot.*, 1921, 8, 464—470; from *Physiol. Abstr.*, 1923, 8, 315).—The change in the electrical resistance of the thallus of *Lamaria Agardhii* was followed when the tissue was immersed in (a) a mixture of 0.61*M*-chromous chloride and 0.52*M*-sodium chloride in equal proportions, and (b) a mixture of 0.22*M*-sodium chromate and 0.52*M*-sodium chromate in equal proportions with enough chromic acid to make the  $p_H$  equal to that of the mixture (a). In the former case the tissue first undergoes an increase in resistance, in the latter a decrease. Ferric chloride brings about a greater increase in resistance than ferrous chloride. This is independent of the hydrogen-ion concentration. W. O. K.

**Permeability of the Cell to Electrolytes.** O. RABEE (*The Botan. Gazette*, 1923, 75, 298—308; from *Physiol. Abstr.*, 1923, 8, 314—315).—Neutral salt solutions of the same osmotic pressure and conductivity as sea-water cause an initial decrease in permeability of *Laminaria* cells, followed by an increase if the valency of the kation is greater than that of the anion, whereas they cause an increase of valency from the start if the valency of the kation is less than that of the anion. If the two are of the same valency, the effect will depend on the relative size of the anions and the density of the accompanying electric charges. A hypothesis, based on consideration of the charge on the membrane is suggested to explain the observed phenomena. W. O. K.

**The Permeability of Living and Dead Cells.** MATILDA MOLDENHAUER BROOKS (*Proc. Soc. Exp. Biol. Med.*, 1922, 20, 39—40; 384—385; *U.S. Public Health Reports*, 1923, 1449—1470; 1470—1477).—The penetration of arsenic from "atoxyl" solutions into the cell sap of *Nitella* increase with  $p_H$  up to  $p_H$  7.5, the most alkaline solution used. The arsenic content of the cell sap of living cells is always less than that of the external solution. With dead cells, the internal and external concentrations are approximately equal. The effect of  $p_H$  on the penetration of arsenic may be due either to its effect on the dissociation of "atoxyl" or to changes in cell permeability. In a series of experiments with *Valonia ventricosa*, it was found that the  $p_H$  of the cell sap is unaffected by acids and remains at 5.2 until all the hydrogen carbonates present have been decomposed. Acids which decompose hydrogen carbonates penetrate slowly, whilst other acids which do not decompose hydrogen carbonates penetrate rapidly. It is inferred from the similarity in the behaviour of live and dead cells that protoplasm is not the only agency regulating the penetration of acids. The cells of *Valonia* are very permeable to carbon dioxide dissolved in sea-water. In the presence of alkali hydrogen carbonates, an increase in the alkalinity of the cell-sap freed from carbon dioxide takes place. The entrance of carbon dioxide and the increase in alkalinity is more marked with potassium

hydrogen carbonate than with sodium hydrogen carbonate. With alkali citrates, acetates, and chlorides, increases in the alkalinity of the cell-sap freed from carbon dioxide are less marked, but the greater influence of the potassium-ion in producing alkalinity is also shown. The above processes do not occur in dead cells.

G. W. R.

**The Synergetic Action of Electrolytes.** O. L. RABER (*Proc. Nat. Acad. Sci.*, 1917, **3**, 682—685; from *Physiol. Abstr.*, 1923, **8**, 315).—*Laminaria* tissue was immersed in solutions of sodium chloride, sodium citrate, and in mixtures of both. The presence of the two ions increases the action of both, so that the resistance of the tissue is lower than would be expected if the effect were additive.

W. O. K.

**Chemistry of Japanese Plants. II. Composition of Fossil Wood.** SHIGERU KOMATSU and Hidenosuke UEDA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1923, **7**, 7—13).—Umoregi, a fossil wood, contains more sulphur and nitrogen than coal and has a carbon and hydrogen content similar to that of peat. It contains: resin, 5—6%, water 17—18%, ash 1%, methylpentosan 1.8%, total polysaccharides 5.1%, lignin 56%, and cellulose 28—30%. By comparing these figures with similar ones for the analysis of the red wood (*Sequoia sempervirens*) from which the umoregi was formed, it is concluded that during fossilisation the wood lost 20% as cellulose and 4% as polysaccharides, gaining, at the same time, 25% as lignin and 2% as resin.

E. E. T.

**Lævulosans in Cereals.** H. COLIN and H. BELVAL (*Compt. rend.*, 1923, **177**, 973—975; cf. this vol., i, 1044).—Rye is the cereal with which lævulosans are to be associated, since they constitute 40% of the dried material in the case of very young grains, and are even present in the ripe grains and in rye flour. Wheat and barley contain smaller quantities (than rye) of lævulosans, but the distribution is similar from the point of view of age of the plant. Lævulosans are present in the stem and immature grains of oats, but not in the ripe grains, or in oatmeal, whilst maize and buckwheat do not contain lævulosans at any stage in their development.

E. E. T.

**Effect of Boric Acid and Borax on the Broad Bean and certain other Plants.** KATHERINE WARINGTON (*Ann. Bot.*, 1923, **37**, 629—672).—In water-cultures, a continual supply of boric acid was found to be essential for the healthy growth of broad bean plants. Beneficial effects were produced at concentrations of 1:12,500,000 to 1:25,000. With higher concentrations, toxic effects were observed. In the absence of boron, death ultimately occurs, but the small amounts of boron shown to be present in the cotyledons of the plant enable it to survive for a short period. Whilst barley does not appear to require boron, certain other plants of the *Leguminosæ* were found to resemble the broad bean. The

function of boron is held to be nutritive rather than catalytic. Application of boric acid under ordinary field conditions is, as a rule, unlikely to be required since small quantities of boron commonly occur in ordinary soils.

G. W. R.

**The Occurrence of Urease.** HENRY E. ARMSTRONG (*Nature*, 1923, 112, 620—621; cf. Werner, this vol., i, 1046; Beijerinck, this vol., i, 1157).—Quotations demonstrate that, contrary to Werner's belief, the existence of urease in the root-nodules of leguminous plants was recognised previously to the publication of the papers cited. The relation of the occurrence of urease to the use of carbamide as a fertiliser is emphasised.

A. A. E.

**Composition of *Monotropia hypopitys*. L. Isolation of a New Methyl Salicylate Glucoside, Monotropitin.** MARC BRIDEL (*Compt. rend.*, 1923, 177, 642—644; cf. this vol., i, 820).—Bourquelot (A., 1896, ii, 540), who showed that *Monotropia hypopitys*, L., contained a glucoside derived from methyl salicylate, conjectured its identity with gaultherin (Schneegans and Gerock, A., 1895, i, 109). This is incorrect, the glucoside present in *Monotropia hypopitys* being now named *monotropitin*. It forms odourless needles, possessing a bitter taste, is non-reducing, has  $[\alpha]_D -57.05^\circ$ , and, after drying in a vacuum at  $50^\circ$  (a process accompanied by a loss of weight of 5.67%), has m. p.  $91.5-92^\circ$  (shrinking at  $88^\circ$ ). Dilute sulphuric acid at  $100^\circ$  affords methyl salicylate and a reducing sugar (possibly an equimolecular mixture of xylose and dextrose).

E. E. T.

**The Cyanogenetic Glucosides.** N. WATTIEZ (*Ann. bull. Soc. roy. Sciences med. natur. Bruxelles*, 1922, 70—77; *Ber. ges. Physiol.*, 16, 211—212; from *Chem. Zentr.*, 1923, iii, 159).—Direct estimation of hydrocyanic acid by distillation always gives smaller results than those obtained from estimating the amount of glucoside (Bourquelot). This is regarded as evidence that in the plants examined, *Prunus laurocerasus*, *P. persicaria*, and *Sambucus nigra*, hydrocyanic acid does not occur in the uncombined state.

G. W. R.

**Essential Oil of *Stirlingia latifolia* from Western Australia.** (*Bull. Imp. Inst.*, 1923, 21, 318—320).—The yield obtained from fresh plants by distillation with steam was 0.75%, but from dried shoots sent to England the yield was only 0.35%. The oil consists almost entirely of acetophenone.

S. I. L.

**Acidity of Highly Basic Soils.** W. T. McGEORGE (*Soil Sci.*, 1923, 16, 195—206).—A study of the behaviour of a number of Hawaiian soils of high basicity, as shown by gross analysis, but of varying actual acidity with different tests for lime requirement. [See, further, *J.S.C.I.*, 1923, 1142A.]

G. W. R.

**Manganese, Aluminium, and Iron Ratio as Related to Soil Toxicity.** R. H. CARR and P. H. BREWER (*Ind. Eng. Chem.*, 1923, 5, 634—637).—Manganese, aluminium, and iron are present as

soluble salts in many soils and in quantities sufficient to be toxic to vegetation; they are readily soluble in 5% potassium thiocyanate solution (cf. A., 1922, ii, 172), yielding a red coloration when iron is present and a green coloration when manganese is present in the manganic form and the solution has been sufficiently basic ( $p_H$  5.5 to remove the red coloration of the ferric thiocyanate. Aluminium ferric and ferrous iron, manganese, calcium hydrogen carbonate (as calcium carbonate), and magnesium are precipitated as hydroxides in the order mentioned, and range in reaction from  $p_H$  4.0 to  $p_H$  10.0 different amounts of limestone added to a soil appear to precipitate some of these elements in the same order. There is but little evidence of toxicity or of a green coloration when 0.006 to 0.008% of manganese is present in the potassium thiocyanate extract of a soil, but 0.015 to 0.03% exhibits distinct toxicity. When a considerable quantity of manganese is present in a soil, as indicated by the formation of a green coloration in the potassium thiocyanate solution, from 40 to 50 c.c. of N/10-alkali solution per 50 g. of soil are required to precipitate the manganese as hydroxide.

W. P. S.

**Native Ferromanganese Ore as a Catalytic Fertiliser.** E. PICADO and E. VICENTE (*Ann. Inst. Pasteur*, 1923, 37, 891—899).—Application of finely ground ferromanganese ore gave increases in the yield of carrots, oats, haricot beans, potatoes, and maize. The optimum application varied from 2 kg. per hectare in the case of maize to 74 kg. per hectare in the case of potatoes. The increase for optimum application varied from 12.56% for maize to 68% for oats. Negative results were obtained with radish and mustard. It is also shown that the alcoholic fermentation of molasses is accelerated by the presence of small quantities of ferromanganese.

G. W. R.

**Organic Phosphorus in Soils.** J. T. AUTEN (*Soil Sci.*, 1923, 16, 281—294).—The Potter and Benton method (A., 1917, i, 76) for the estimation of organic phosphorus is held by the author to give fairly accurate results. Considerable amounts of organic phosphorus were found in the soils examined. The mode of occurrence of organic phosphorus in soils is discussed. It is concluded that it does not exist in appreciable amounts as nucleic acid, phytin, lecithin, or pyrimidine nucleotides. Organic phosphorus added to soils is probably hydrolysed and combined as a calcium-magnesium or other metallic salt of an amphoteric organic complex.

G. W. R.

**Estimation of the Relative Solubility of Phosphoric Acid in Soils.** O. LEMMERMANN and L. FRESSENIUS (*Z. Pflanz. Düng.*, 1923, 2, 363—369).—From a comparison of different soils, some of which respond and others of which do not respond to phosphatic fertilisers, it is concluded that the relative solubility of the phosphoric acid of soils, i.e. the proportion of the total phosphoric acid, soluble in 1% citric acid, can give information as to the need or otherwise for phosphatic applications.

G. W. R.







